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PROCEEDINGS

OF THE

AMERICAN ACADEMY

OF

ARTS AND SCIENCES.

VOL. XXI.

PAPERS READ BEFORE THE ACADEMY.

INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATION FROM THE RUMFORD FUND.

I.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XX. — ON THE EFFECT OF TEMPERATURE ON THE VISCOSITY OF AIR.

BY SILAS W. HOLMAN.

Communicated May 13, 1885.

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THE investigation described in the present paper is a continuation of the work done on the same subject by the author in 1876.* The experimental portion of the work consists of about 250 independent measurements of the viscosity of air and 140 of carbon dioxide (carbonic acid), besides somewhat extended incidental researches on thermometry. The temperature ranges for air were from 0° to 124° C.; for carbonic acid, from 0° to 225° C. The plan adopted at the outset was to make some study of the method and of the best form of apparatus; then to proceed to the study of several gases which have been

* On the Effect of Temperature on the Viscosity of Air, Proc. Amer. Acad. Arts and Sci., xii. (1876), p. 41. Phil. Mag., iii. 81 (1876). Wied. Beibl., i. 222.

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already well investigated, either in regard to their viscosity or other properties, making measurements of the viscosity at temperature intervals of about 20° from low to high temperatures. But the laborious nature of the observations, and the large amount of time demanded by the observations and their reduction, have rendered the fulfilment of the plan impossible for one whose available time has been fully occupied with laboratory instruction. It will be seen that the last of the observations given were made in April, 1880. Since that date it has been wholly inconsistent with the author's duties and health to continue the work, and the incomplete results are now presented in the hope that, despite their limited range, they may be a contribution of some permanent value to the subject treated.

The expenses of the investigation have been mainly defrayed by an appropriation granted by the American Academy of Arts and Sciences from the Rumford Fund for researches on Light and Heat.

The objects of the investigation were concisely stated in the paper of 1876. The extension of the work was looked to for the development of data which not only should furnish another experimental check on the deductions of the kinetic theory of gases, but should provide material of sufficient precision (approximating to that with which the coefficient of expansion of gases is known) to serve as a part of that experimental basis on which the complete theory of gases, and indeed of molecular physics in general, must eventually rest. The critical review of the method, given at the end of the paper, is intended to furnish the material for the formation of a judgment as to how far this object has been fulfilled in the case of the gases investigated.

Apparatus.

The apparatus used is shown in the schematic section given by the accompanying cut. It is in principle the same as that used in the former measurements. The dried gas is transpired successively through two glass capillaries of about 30 cm. in length, from a space containing the gas at a measured pressure to another space from which the gas is continuously exhausted as fast as it enters, and which is thus maintained at a constant and measured pressure. The pressure of the gas in the intermediate space is also measured. The capillaries are maintained at known or measured constant temperatures, AB being usually packed in finely pounded ice, and DC being in a jacketed double oil-bath, of which the temperature is maintained nearly constant by regulating the flame of the gas-burners, and is measured by the thermometer with its

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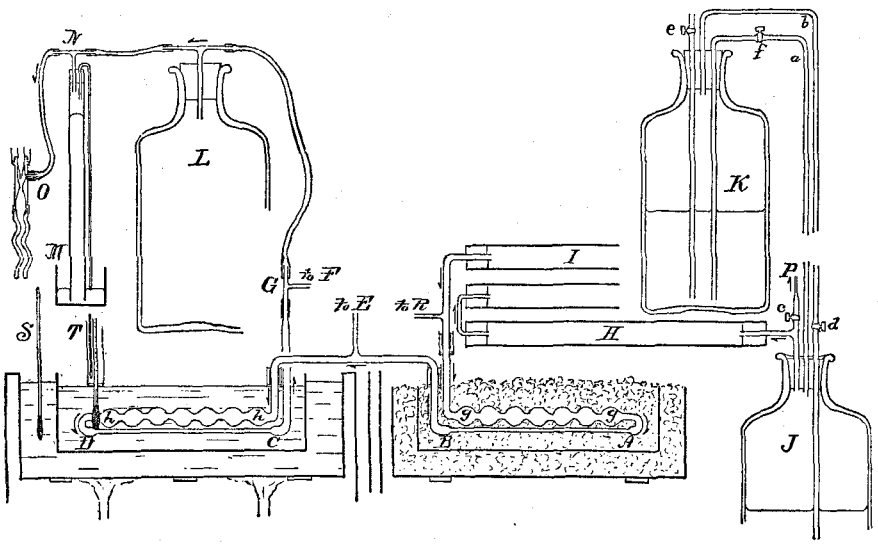
bulb at D, the entrance to the capillary. Both inner and outer oil baths are continuously stirred by an agitator moved to and fro through the troughs by a water motor with connections not shown in the sketch. This arrangement maintained temperatures as high as 225° constant within about 0°.5 in most measurements, and so nearly uniform throughout the trough that no perceptible difference could be found at various points along the capillary. A thermometer at S in the outer bath served to adjust the lamps so that their heating should be such as to maintain a nearly constant temperature. Automatic thermo-regulators were tried, but were found in general to be quite as much of a disadvantage as benefit, and were abandoned.



The details of the apparatus will be described, beginning at the point where the gas enters. When air was used, the laboratory air was drawn in through caustic potash to remove the carbonic acid, and through concentrated sulphuric acid, fused chloride of calcium, and anhydrous phosphoric acid in the tubes H and I, which are further described at I. 2, p. 29. When carbonic acid was used, the gas was formed by the action of hydrochloric acid on marble, was purified by washing in water, dried, and freed from hydrochloric acid by passing through tubes of pumice coated with anhydrous copper sulphate. The gas was then drawn through P into J by withdrawing the concentrated sulphuric acid from J into K, as about to be described, and was there held for use. When a measurement was in progress, the gas in J, being

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slowly and uniformly displaced by the sulphuric acid returning from K, passed into and through H and I, arranged as already described. The glass bottles J and K held each about 10 litres, and one was filled with concentrated sulphuric acid. K was placed about a meter above J. The two were connected by two glass tubes, a and b, each containing a stop-cock, and had other tubes arranged as shown in the sketch. To withdraw the sulphuric acid from J into K, and to replace this by the CO_2, it was necessary simply to connect P to the gas-holder or generator, to close e and f, to open c, to exhaust the air from K by an aspirator, and, opening the cock in b, to allow the H_2SO_4 to be transferred to any desired extent. This being accomplished, d and c were closed and the generator disconnected. When a measurement is in progress, the CO_2 passing at a uniform rate from J through Q must be replaced by sulphuric acid from K through a. This flow is regulated by a tangent screw motion on the cock f, until the liquid drops or runs into J at such a rate as to displace not only the necessary amount of CO_2, but slightly more than this, the excess escaping slowly through c and a fine orifice at P. This arrangement maintains an almost constant pressure in J, and, as the pressure is thus always outward, there can be no inward leakage of air either during the measurements or at other times. The gas, after passing, always with this slight excess of pressure within, through $H I$, enters the glass bulbs $g\,g$, and the pressure p_1 at entrance is measured by the barometric height at the time plus the pressure indicated by the gauge at R, read by the cathetometer. The bulbs $g\,g$ were spherical enlargements of about three centimeters in diameter of a glass tube of about half a centimeter in diameter. The contents of these bulbs would be transpired by the capillaries once in about fifteen minutes. The tube $g\,g$ and the capillary were connected into one piece at A by melting them together, and a similar solid connection was made at B to an exit tube. The tubes $C D$ and $h\,h$ were similar in all respects to $A B$ and $g\,g$, the capillaries being of very nearly the same length, and cut from the same piece of tubing, which was one of those used in the experiments of 1876. The connections of these tubes to the other tubing of the apparatus, as shown in the drawing, were all made as described in I. 3, p. 29. The tube connecting B to $h\,h$ was of about 3 mm. internal diameter and 50 cm. length, and at its middle point contained a branch, which extended, with one joint of the kind described, to the gauge E, which in connection with the barometer served to measure p_2. The gas at exit from C passed about 50 cm. of 3 mm. tubing to the point G, where a side branch led to the gauge F, which gave the pressure p_3. Passing by G,

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the gas moved forward past *N* to the aspirator *O*,* and then escaped. The bottle *L*, of about 10 litres' capacity, sometimes two bottles each of that volume, connected between *G* and *N*, served to reduce the rate of pressure fluctuations arising from irregularities in the aspiration. At *N* was connected the pressure-regulator, which I will describe in detail, as it is so far as I know wholly new and is available for many purposes.

The aspirator under a given head of water can exhaust at a definite rate, maintaining a certain exhaustion; if the head be increased or lessened, the rate of exhaustion will be increased or diminished, and thus if the leakage into the exhausted space, as through the capillaries in this case, be sensibly constant, the pressure in the exhausted space must diminish or increase. It is often impracticable, as it was for me, to maintain a constant head of water, and some means is therefore necessary to overcome this irregular action. The arrangement used was that shown in the sketch. A large glass tube *M*, open at both ends, stands upright in an open mercury trough of considerably larger dimensions. Into its top is inserted a rubber stopper with two borings, through one of which passes one arm of a T joint whose other two arms are connected respectively with the aspirator and the vessel to be exhausted. Through the other boring passes a tube of 1 mm. to 2 mm. diameter bent twice at right angles, and dipping into the mercury in the trough. Suppose that the vessel to be exhausted is closed — the apparatus covers cases ranging from this to a leakage of about half the rate of exhaustion of which the pump is capable — and the aspirator set in operation. As the exhaustion proceeds, the mercury rises equally in both large and small tubes until the mercury in the trough drops below the point of the latter, whereupon, as soon as the excess of external pressure is sufficiently great to overcome the friction of the mercury, the column in the fine tube rises rapidly and flows over into the upper part of the large tube and upon the mercury surface in it. This overflow is of course immediately followed by an inrush of air through the open point, and a consequent sudden lowering of the mercury in the large tube with a corresponding rise of level in the trough which closes or partly closes *D*. This first sudden action is followed by several of lessening violence, and a steady condition is soon reached, in which there is a continuous inflow of air and small drops of mercury at the point, the

* Richard's jet aspirator was used. See Amer. Jour. Sci., [3], viii. 200; Chem. News, xxxiv. 141; Trans. Amer. Inst. Mining Eng., vi. 492 (1879).

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proportion between the two depending upon the relation between the sizes of the tubes, the capacity of the aspirator, and the supply of gas from the vessel to be exhausted. If a fluctuation occurs in either the rate of the aspiration or the supply of gas to be exhausted, a greater or less proportion of air will be taken in, with a corresponding but very small change of the pressure within the apparatus. For the successful working of the apparatus a proper proportioning of parts to the work to be done is of course necessary, and this is mainly to be accomplished by varying the size of the point to which the fine tube is drawn out. The sensitiveness of the apparatus may be increased by using a U tube, instead of a vertical straight tube with cistern, and allowing the fine tube to extend into the open arm of this tube. A stricture at some point of the U reduces the too sudden fluctuations. Various other modifications will readily suggest themselves to persons using the apparatus. The regulator is of course of service in other ways than merely rendering uniform the action of the aspirator. It is possible to maintain with it a constant exhaustion of any desired amount up to the full exhaustion which the aspirator can produce when working under the smallest head of water likely to occur; and in the form of a U tube, with various lengths of tube *DE*, to be inserted at *A* and raised or lowered, it affords a very convenient means of varying the exhaustion at will.

Procedure in Measurements.

The first operation is thoroughly to dry the apparatus and fill it with pure dry gas. This was accomplished by repeated exhaustion and refilling of all necessary parts of the tubing, gauges, etc., none but thoroughly dry gas being admitted. This operation was repeated on each separate day of measurement so that any error from slight leakage or diffusion of either air or moisture should be avoided. On the first introduction of the dry air or carbonic acid, the further precaution was taken to run the apparatus under quite high exhaustion for many hours consecutively; and in all cases, on each day of measurement, the apparatus was run for an hour or more before any readings were taken.

The procedure in measurement was as follows. The aspirator was set in operation, *J* being full of the gas. The generator and purifiers were connected at *P*, and the cock *c* opened, *f* remaining closed, so that the supply of gas came from the generator; the temperature of *DC* was regulated, the stirrer being in continuous operation; the ice-bath

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was placed around AB, the regulator at N adjusted, and the transpiration allowed to proceed until the gauges E and F were nearly stationary. Then c was closed, and f opened and adjusted so that the reading of R slowly increased, whereupon c was again opened for the slow escape of the gas and the maintenance of a constant initial pressure p_1. The transpiration was allowed to proceed until E, F, and R were sufficiently near stationary, when readings of the mercury columns by the cathetometer and of the thermometers were taken systematically. After a complete set of readings had been thus obtained, the apparatus was thoroughly inspected and a second set made ; and so on until the number was deemed sufficient, whereupon the temperature of DC was changed or the pressure modified as desired. The results thus obtained furnished, on reduction, the values of p_1, p_2, p_3, and t for the computation of the ratio of the coefficient of viscosity at the higher temperature to that at 0° C., the further requirements being the constants $\frac{R_2^4 \lambda_1}{R_1^4 \lambda_2} = K$ for the tubes, R_1 and λ_1, R_2 and λ_2, being the radius and length respectively of the tubes AB and CD, as shown at page 9. This value of K was found from measurements similar in all respects to those just described, except that the tubes AB and CD were both surrounded with ice at the same time.

The apparatus was also arranged to place DC in steam. When left at night for subsequent use, an outward pressure was created in all parts of the apparatus.

Experimental Results.

The results will be here given as they were for convenience classified during the progress of the work, viz. with dry air in five series, with carbonic acid in two series. The method of reduction of the results is given at page 26, and in my first paper.

Air.

First Series. — This consists of the twenty-one measurements made in 1876 as given at page 49 of the article referred to, and gives as a mean result of the ten measurements of $\frac{\eta_1}{\eta_2}$ as shown in Table I. below, the value $y = \frac{\eta_1}{\eta_2} = 1.234$, with an average deviation* of 0.044,

* Let a_1, a_2, a_3, . . . a_n, be a series of measurements of the same quantity, and let m be their arithmetical mean; then $a_1 - m = d_1$, $a_2 - m = d_2$, $a_3 - m = d_3$, &c., will be the deviation of these measurements from their

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or about four per cent. A glance at the page referred to will show, however, that of these ten measurements but six were at the temperatures of 0° and 100° respectively. These six as shown in Table II. give the mean

$$y = \frac{\eta_{100}}{\eta_0} = 1.270 \pm a.d.\ 0.005,$$

and this mean I shall use in comparing this series with the later ones, omitting those results obtained at temperatures between 0° and 100°, because the want of certainty in the temperature measurements would render the labor of the necessary computations fruitless.

TABLE I.

No.	$\frac{\eta_1}{\eta_2}$.	d.
2	1.083	—.151
7	1.212	—.022
8	1.206	—.028
9	1.215	—.019
11	1.272	+.038
12	1.267	+.033
13	1.271	+.037
14	1.273	+.039
18	1.277	+.043
21	1.259	+.025
	1.234	0.044

TABLE II.

No.	$\frac{\eta_1}{\eta_2}$.	d.
11	1.272	+.002
12	1.267	—.003
13	1.271	+.001
14	1.273	+.003
18	1.277	+.007
21	1.259	—.011
	1.270	0.005

Second Series. April, 1878. — In making a study of the best forms of apparatus, a careful trial was given to capillaries in the form of a helix, as these facilitate the maintenance of constant and uniform temperatures of the bath, and render the use of longer and larger tubes possible. The coils were successfully made by winding the tubing, as it was drawn from the tube of the glass-worker, upon a wooden drum. The second series was made with a pair of such coils, and consisted of only eight measurements. The results in the measurements of K were so wholly discordant, that they were at once rejected.

Third Series. — A second pair of smaller coils was mounted in a manner similar to that just described, and with the same general results, showing the coils to be utterly useless; probably, as was to

---

mean, and $\frac{d_1 + d_2 + d_3 + \ldots . d_n}{n}$ will be the average deviation, if, in the summation of the numerator, the values of d_1, d_2, &c. be taken arithmetically, without regard to algebraic sign.

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be anticipated, because of changing curvature of the coils owing to expansion or change of position. Several straight capillaries were also studied, varying in size and in the form of tube employed for heating the gas. These experiments covered the whole 126 measurements of this series, and resulted in the selection of the form and size given in the general description of the apparatus at page 2. No systematic study was made, however, of the effects of the proportions of the tube on the law of the transpiration, though the apparatus seems well adapted for that purpose.

Fourth Series. October, November, and December, 1878. — The capillaries used in this series were those described in the general account of the apparatus at page 2; viz. straight tubes of about 30 cm. in length and 0.0110 cm. in diameter, and were cut from tube I of the apparatus of 1876. The mercury columns were read to 0.1 mm. by a reading telescope from steel millimeter scales placed behind the gauges. Corrections were applied to these scales, but the precision of reading was much less than in the fifth series; the temperature measurements were also somewhat less precise, and the whole series should receive much less weight, owing to the conditions under which it was taken, than the fifth series on air, or the second series on carbonic acid. Table III gives the results obtained.

In the Table the letters heading the columns have the same meaning as elsewhere throughout the paper. The pressures p_1, p_2, &c. are given in millimeters of mercury at 0° C. at Boston. The column headed "Mean $\frac{\eta_2}{\eta_1}$ or K," contains the mean of the group of values of $\frac{\eta_2}{\eta_1}$, or of K, immediately preceding, and a similar statement is true of the column headed "Mean t_2."

The results from No. 49 onwards are of much greater precision than those preceding, chiefly from the use of greater pressures, which increased the precision of measurement. Measurements 49 to 99, when combined by the method of least squares, give for constants in the empirical equation

$$\frac{\eta_t}{\eta_0} = \frac{\eta_2}{\eta_1} = 1 + At + Bt^2$$

the values, between the limits $t = 0°$ and $t = 100°$,

$$A = 0.002821, \quad \text{and} \quad B = -0.00000149.$$

These values, however, I have regarded as entitled to so much less weight than those of the fifth series for air, that they are given here

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TABLE III. — Air. Fourth Series.

No.	t_1.	t_2.	Mean t_2.	$\frac{\eta_2}{\eta_1}$.	Mean $\frac{\eta_2}{\eta_1}$ or K.	K.	p_1.	p_2	p_3.
	°	°	°				mm.	mm.	mm.
1	21.4	21.4	....	....	....	1.0571	753.8	639.3	507.8
2	100.0	100.0	....	....	....	1.0471	753.8	638.9	505.3
3	99.94	0.0	....	1.265	1.0521	....	758.5		
4	99.94	0.0	....	1.272	....	....	758.5	610.2	511.8
5	99.94	0.0	....	1.265	....	....	758.5	610.1	510.8
6	99.94	0.0	....	....	....	....	758.5	610.1	510.8
7	99.94	0.0	....	1.266	....	....	758.5	546.0	382.9
8	99.94	0.0	....	1.266	....	....	758.5	546.0	382.9
					1.266				
9	0.0	0.0	....	....	....	1.0542	764.3	645.0	506.5
10	0.0	0.0	....	....	....	1.0574	764.2	645.2	507.6
11	0.0	0.0	....	....	....	1.0585	764.0	645.1	507.8
12	0.0	0.0	....	....	....	1.0517	764.2	606.6	403.1
13	0.0	0.0	....	....	....	1.0520	764.3	569.8	279.3
					1.0548				
21	0.0	16.46	....	1.0308	....	....	763.4	698.3	623.5
22	0.0	16.48	....	1.0380	....	....	763.4	698.5	623.4
23	0.0	16.50	....	1.0355	....	....	763.4	698.2	622.9
			16.48		1.0348				
24	0.0	28.19	....	1.0704	....	....	762.5	699.2	620.5
25	0.0	28.32	....	1.0718	....	....	762.5	699.3	620.6
26	0.0	29.02	....	1.0655	....	....	761.9	698.2	619.1
27	0.0	29.18	....	1.0679	....	....	761.5	697.9	618.7
28	0.0	28.98	....	1.0707	....	....	761.5	698.3	619.5
			28.74		1.0693				
29	0.0	30.49	....	1.0744	....	....	761.5	698.6	619.5
30	0.0	30.41	....	1.0735	....	....	761.5	698.6	619.6
31	0.0	30.30	....	1.0774	....	....	761.4	698.2	618.5
32	0.0	30.12	....	1.0810	....	....	761.4	699.0	620.2
33	0.0	30.06	....	1.0787	....	....	761.4	698.8	620.3
			30.28		1.0760				
34	0.0	37.05	....	1.0945	....	....	761.0	699.6	619.3
35	0.0	37.15	....	1.1016	....	....	760.9	699.9	619.6
36	0.0	37.30	....	1.1035	....	....	760.8	700.2	620.3
37	0.0	37.35	....	1.0982	....	....	760.8	700.2	620.7
			37.21		1.0995				
38	0.0	53.40	....	1.1283	....	....	755.8	698.1	616.3
39	0.0	53.60	....	1.1277	....	....	755.8	698.1	616.3
40	0.0	53.96	....	1.1404	....	....	755.8	697.9	614.7
41	0.0	54.11	....	1.1456	....	....	755.8	697.8	614.0
			53.77		1.1355				
42	0.0	46.28	....	1.1318	....	....	755.3	695.4	611.8
43	0.0	46.68	....	1.1180	....	....	755.0	693.9	609.4
			46.48		1.1249				
44	0.0	56.26	....	1.1432	1.1432	....	754.8	695.4	608.9
45	0.0	68.03	....	1.1740	1.1740	....	754.8	697.4	608.5
46	0.0	66.93	....	1.1725	1.1725	....	754.8	697.2	608.1
47	0.0	67.88	....	1.1752	....	....	755.0	697.0	607.9
48	0.0	67.83	....	1.1748	....	....	755.0	696.8	606.5
	Tube I.	remounted	67.86		1.1750				
49	0.0	0.0	....	....	....	....	759.2	557.0	238.0
50	0.0	0.0	....	....	....	....	759.2	557.0	238.0
51	0.0	0.0	....	....	....	1.0517	759.3	556.7	237.5
52	0.0	0.0	....	....	....	1.0520	759.3	556.5	236.7
53	0.0	0.0	....	....	....	1.0517	759.9	556.1	232.9
54	0.0	0.0	....	....	....	1.0522	759.9	556.1	232.8
					1.0519				

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TABLE III. — *Continued.*

No.	t_1.	t_2.	Mean t_2.	$\frac{\eta_2}{\eta_1}$.	Mean $\frac{\eta_2}{\eta_1}$ or K.	K.	p_1.	p_2.	p_3.
	°	°	°				mm.	mm.	mm.
55	0.0	42.80	....	1.1202	....	....	761.4	586.7	232.9
56	0.0	42.84	....	1.1200	....	....	761.5	586.6	232.0
57	0.0	42.84	....	1.1187	....	....	761.6	586.7	232.9
58	0 0	42.95	....	1.1216	....	....	762.0	587.1	231.7
59	0.0	42.95	....	1.1216	....	....	762.0	587.1	231.7
			42.88		1.1204				
60	0.0	0.0	....	....	....	1.0526	760.4	556.6	234.1
61	0.0	0.0	....	....	....	1.0506	760.3	556.6	233.4
62	0.0	0.0	....	....	....	1.0535	760.1	555.1	228.5
63	0.0	0.0	....	....	....	1.0524	760.1	555.2	228.4
64	0.0	0.0	....	....	....	1.0498	759.9	555.6	229.1
65	0.0	0.0	....	....	....	1.0504	759.9	555.6	229.4
66	0.0	0.0	....	....	....	1.0507	759.9	555.5	229.1
					1.0514				
67	0.0	72.55	72.55	1.1913	1.1913	....	760.8	602.3	229.6
68	0 0	12.57	....	1.0372	....	....	754.3	559.5	221.5
69	0.0	12.67	....	1.0366	....	....	754.3	559.3	220.6
70	0.0	12.77	....	1.0371	....	....	754.3	559.4	220.6
71	0.0	12.92	....	1.0368	....	....	754.2	559.3	220.3
72	0.0	12.92	....	1.0365	....	....	754.1	559.2	220.3
73	0.0	12.92	....	1.0365	....	....	754.1	559.2	220.3
			12.80		1.0368				
74	0.0	21.50	....	1.0583	....	....	753.9	565.0	221.1
75	0.0	21.15	....	1.0589	....	....	753.8	565.2	222.9
76	0.0	20.85	....	1.0599	....	....	753.7	564.3	218.5
77	0.0	20.65	....	1.0602	....	....	753.7	564.4	219.3
78	0.0	20.40	....	1.0582	....	....	753.7	563.4	215.6
			20.91		1.0591				
79	0.0	20.15	....	1.0557	....	....	753.7	563.0	215.4
80	0.0	19.80	....	1.0561	....	....	753.7	562.9	215.4
81	0.0	19.65	....	1.0541	....	....	753.7	562.6	215.3
			19.87		1.0553				
82	0.0	40.01	....	1.1100	....	....	753.7	575.9	214.0
83	0.0	39.91	....	1.1116	....	....	753.8	576.1	214.0
84	0.0	39.88	....	1.1081	....	....	753.8	576.0	214.0
85	0.0	39.93	....	1.1111	....	....	754.3	576.5	214.5
			39.93		1.1102				
86	0.0	62.64	....	1.1690	....	....	754.8	590.1	214.2
87	0.0	62.59	....	1.1699	....	....	754.8	590.1	213.8
88	0.0	62.39	....	1.1706	....	....	754.8	590.1	213.8
89	0.0	62.34	....	1.1687	....	....	754.9	590.0	213.9
90	0.0	62.34	....	1.1684	....	....	754.9	590.0	214.1
			62.46		1.1693				
91	0.0	79.92	....	1.2174	....	....	755.4	600.2	214.3
92	0.0	80.02	....	1.2159	....	....	755.4	600.1	214.3
93	0.0	79.62	....	1.2170	....	....	755.4	600.1	214.3
94	0.0	79.32	....	1.2149	....	....	755.5	599.9	214.4
95	0 0	79.32	....	1.2143	....	....	755.5	599.8	214.1
96	0.0	79.27	....	1.2134	....	....	755.6	599.8	214.2
			79.58		1.2155				
97	0.0	99.66	....	1.2655	....	....	751.2	606.0	210.3
98	0.0	99.66	....	1.2657	....	....	751.2	605.2	204.0
99	0.0	99.66	....	1.2685	....	....	751.2	668.2	502.9
			99.66		1.2666				

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merely as a satisfactory and important check upon the further results of that series. The equation deduced from this latter series, I regard as best representing my measurements on dry air. It will be noticed, on comparing the two series, that the greatest deviation of the two series is at 100°, where it amounts to less than 0.4 per cent.

Measurements 1 and 2 were taken during preliminary trials of the apparatus. In 3 to 8 the first capillary was in boiling water, the second in ice, this reversal of the usual sequence of temperatures being made in order to test the apparatus. The mean of these five measurements (the sixth having been rejected when made, as having been taken before the static condition of the process was reached) gives

$$y = \frac{\eta_{100}}{\eta_0} = 1.267 \pm a.d.\ 0.002.$$

The above equation gives for $t = 99°.94$

$$\frac{\eta_t}{\eta_0} = 1.2666,$$

and the direct observation made, as were all those from which the equation is derived, with the first capillary at 0°, gives as the mean at 99°.66

$$\frac{\eta_t}{\eta_0} = 1.2666.$$

The close agreement of these numbers seems to indicate a freedom from constant error of any considerable magnitude in the value of K and in the expansion correction to this value.

Fifth Series. April, 1880.— This series was taken with the apparatus as described at page 2, immediately after the completion of the second series with carbonic acid. The measurements were made under as favorable conditions as any of this paper, and are of greater weight than all of the others upon air. The full data for the computation of these results are given in Table IV. in such form that a recomputation, in so far as relates to those portions subject to possible modification of such amount as to materially change the result, may at any time be made. The value of K used was the same as that used for the second series of carbonic acid.

These measurements may be divided according to temperatures into six groups, and are very concordant except that the sixth group shows a deviation of about 0.6 per cent from the value which the other five groups would indicate at that temperature. There appears

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TABLE IV. — Air. Fifth Series.

No.	p_1-p_2.	p_1+p_2.	p_3-p_3.	p_2+p_3.	a.	t_2.	$\frac{\eta_2}{\eta_1}$.	Computed $\frac{\eta_2}{\eta_1}$.	d.
1	92.31	1418.23	113.29	1212.63	.0036693	13.70	1.0374		
2	92.26	1417.90	113.37	1212.27	.....	13.93	1.0378		
3	92.15	1417.71	113.35	1212.21	.....	14.21	1.0378		
					Means =	13.947	1.0377	1.0383	—.0006
4	83.93	1423.93	122.09	1217.91	.0036694	42.60	1.1180		
5	83 86	1423.50	122.13	1217.51	.....	43.04	1.1178		
6	83.81	1423.35	122.27	1217.27	.....	43.30	1.1187		
7	83.98	1422.78	122.41	1216.39	.....	43.17	1.1178		
8	83.98	1422.44	122.25	1216.21	.....	42.76	1.1179		
					Means =	42.974	1.1180	1.1176	+.0004
9									
10	77.39	1425.25	128.88	1218.98	.0036694	67.74	1.1861		
11	77.34	1425.16	128.76	1219.06	.....	67.74	1.1859		
12	77.34	1425.08	128.83	1218.91	.....	67.94	1.1831		
					Means =	67.81	1.1850	1.1850	.0000
13	72.44	1429.96	133.48	1224.04	.0036695	88.67	1.2381		
14	72.29	1430.11	133.59	1224 23	.....	88.64	1.2419		
15	72.20	1430.14	133.49	1224.45	.....	88.85	1.2419		
16	72.20	1429.96	133.59	1224.17	.....	88.92	1.2424		
					Means =	88.77	1.2411	1.2415	—.0004
17	70.20	1441.48	136.41	1234.87	.0036696	99.69	1.2684		
18	70.28	1441.22	136.35	1234.59	.....	99.02	1.2686		
19	70.23	1440.51	136.58	1233.70	.....	98.93	1.2716		
20	70.05	1440.43	136.11	1234.27	.....	99.41	1.2695		
21	70.05	1440.19	136.14	1234.00	.....	99.03	1.2710		
22	70.10	1440.10	136.16	1233.84	.....	99.18	1.2695		
					Means =	99.21	1.2698	1.2696	+.0002
23	64.94	1446.20	141.17	1240.09	.0036697	124.61	1.3321		
24	64.86	1446.46	141.21	1240.39	.....	124.36	1.3350		
25	65.12	1446.42	140.95	1240.35	.....	124.17	1.3279		
26	64.98	1446.72	141.02	1240.70	.....	124.22	1.3314		
27	65.12	1446.94	140.96	1240.86	.....	124.69	1.3264		
					Means =	124.41	1.3306	1.3368	—.0062

to be in this group some considerable constant error, due probably to a mistake in the reading of the themometer which was a different one, from that used in the preceding groups. The deviation is so large that I have thought it best to reject the sixth group wholly in the computation of the empirical equation for this series on air. I fully recognize that this rejection may be considered somewhat arbitrary, and also that the retention of the sixth group would make the accordance between the fourth and fifth series greater than now; but I am so fully satisfied that there is some mistake in the rejected group

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that I unhesitatingly lay it aside. I thus obtain by the method of least squares for measurements 1 to 22 on dry air, 5th series,

$$\frac{\eta_t}{\eta_0} = 1 + 0.002751\, t - 0.00000034\, t^2,$$

between the temperature limits of 0° and 100°C. The last column of the table, headed d, gives the deviations of the observed means from the values of $\frac{\eta_t}{\eta_0}$, computed for the same temperatures t_2 by the preceding equation and given in the ninth column. The average deviation of the means from the equation is thus only 0.0003, or about 0.03 per cent, for the first five means, the deviation of the sixth mean being ten times the next greatest deviation. The average deviation of the individual observations from their respective means, disregarding the correction corresponding to the slight differences of the observed temperatures from the mean, is 0.0012 or about 0.1 per cent.

Carbonic Acid. CO_2.

First Series. — 21 measurements were made in January, 1879, after the close of the fourth series on air, and with the same apparatus, with the addition of the necessary apparatus for holding the gas. The precision of the results was less than in the fourth series for air, chiefly because of the somewhat greater complication of the apparatus for the supply of the gas. The results are of little value, but are given as a check on the second series. The pressures were about the same as in Nos. 49 to 98 of the fourth series on air. The temperature t_1 of the first capillary was always 0° C. The following Table V. gives the mean results. The coefficient of expansion used was 0.003699, a value taken from Regnault's work by interpolation for the actual pressure p_2, under which the expansion occurs.

The column headed n gives the number of measurements going to make up the corresponding means.

TABLE V. — CO_2. First Series.

n.	t_2.	$\frac{\eta_2}{\eta_1}$.	Computed $\frac{\eta_2}{\eta_1}$.
8	29.61	1.103	1.108
5	48 56	1.178	1.175
8	100.09	1.324	1.351

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Second Series. — 120 measurements were made from January to April, 1880, with the complete apparatus as described at pages 2 and 9. The thermometers used were Casella 32378, Baudin 7335 up to 180°, and Baudin 7789 above 200°. The first 20 measurements were preliminary, being made with various tubes and forms of apparatus before satisfactory forms were obtained. The remainder are given in the following table. In all cases $t_1 = 0°$.

TABLE VI. — CO_2. SECOND SERIES.

No.	p_1.	p_2.	p_3.	K.	Mean K.
1	784.08	720.53	653.77	1.0422	
2	786.69	720.17	653.99	1.0918	
3	787.48	721.58	654.10	1.0737	
4	785.44	722.30	654.54	1.0204	
5	790.61	724 59	654.84	1.0397	
6	758.59	700.78	640.07	1.0364	
7	758.17	700.30	639.71	1.0638	
8	757.60	699.82	639.23	1.0380	
9	757.15	699.27	638.57	1.0381	
10	773.74	707.56	637.41	1.0390	
11	774.14	707.50	636.92	1.0169	
12	780.55	718.34	652.49	1.0330	
13	780.74	718.12	652.18	1.0387	
					1.0440
14	748.64	699.58	649.47	1.0510	
15	748.45	699.99	649.37	1.0276	
16	748.27	699.72	649.27	1.0330	
17	748.52	699.55	648 81	1.0365	
18	748.37	699.34	648.75	1.0408	
19	748.19	699.33	648.68	1.0359	
					1.0375
20	771.58	614.35	409.82	1.0402	
21	771.62	614.36	409.70	1.0376	
22	771.66	614.35	409.57	1.0399	
23	771.67	614.28	409.22	1.0394	
24	772.11	614.50	409.16	1.0397	
25	772.38	614.57	408.98	1.0401	
					1.0395
26	770.73	611.24	400.91	1.0353	
27	770.55	610.67	400 83	1.0404	
28	770.37	610.55	400.81	1.0404	
29	771.92	701.15	625.09	1.0335	
30	771.71	700.74	624.68	1.0366	
31	771.50	700.54	624.90	1.0419	
32	767.36	705.39	640.08	1.0386	
33	767.46	705.46	640.22	1.0394	
34	766.90	705.13	639.89	1.0362	
35	766.80	705.01	639.71	1.0357	
36	767.34	712.33	655 13	1.0406	
37	767.29	712.39	655.18	1.0383	
38	766.95	712.12	654.91	1.0370	
					1.0380

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TABLE VI. — CO_2. SECOND SERIES. — *Continued.*

No.	p_1.	p_2.	p_3.	100 a.	t_2.	$\frac{\eta_2}{\eta_1}$.	Mean t_2.	Mean $\frac{\eta_2}{\eta_1}$.	Computed $\frac{\eta_2}{\eta_1}$.
39	746.72	693.79	630.67	0.37047	17.62	1.0688			
40	746.53	693.62	630.49		17.87	1.0684			
41	746.18	693.31	630.10		18.09	1.0696			
42	745.93	692.94	629.77		18.29	1.0658			
43	745.64	692.71	629.47		18.62	1.0669			
							18.10	1.0679	1.0666
44	745.41	696.50	628.79	0.37053	41.15	1.1468			
45	745.64	696.68	629.03		41.28	1.1472			
46	745.97	697.01	629.24		40.86	1.1481			
47	746.41	697.32	629.70		40.86	1.1426			
48	746.73	697.75	630.22		40.87	1.1438			
49	747.45	698.54	630.98		40.87	1.1461			
							40.98	1.1458	1.1485
50	769.40	723.90	653.79	0.37071	59.02	1.2125			
51	769.56	724.17	653.75		59.30	1.2197			
52	769.49	724.18	654.04		59.54	1.2164			
53	769.47	724.20	654.31		59.50	1.2163			
54	769.25	723.90	654.43		58.93	1.2064			
55	769.23	723.89	654.25		58.72	1.2102			
56	769.26	724.01	654.68		58.96	1.2068			
							59.14	1.2126	1.2119
57	774.14	732.22	659.65	0.37077	79.56	1.2847			
58	774.07	732.31	659.96		79.58	1.2860			
59	773.93	732.35	660.33		79.72	1.2857			
60	773.66	732.17	660.48		79.73	1.2829			
							79.65	1.2848	1.2820
61	773.71	735.84	662.96	0.37081	99.67	1.3550			
62	773.62	735.83	663.22		100.17	1.3514			
63	773.50	735.77	663.52		100.24	1.3468			
64	773.78	736.13	663.86		100.60	1.3490			
							100.17	1.3506	1.3508
65	780.77	745.42	670.80	0.37087	119.11	1.4147			
66	780.70	745.31	670.68		119.20	1.4129			
67	780.32	745.04	670.69		119.27	1.4120			
68	779.81	744.65	670.56		119.37	1.4119			
69	779.58	744.58	670.24		119.55	1.4223			
							119.30	1.4148	1.4139
70	770.66	738.34	663.10	0.37083	141.53	1.4774			
71	770.52	738.18	662.91		141.89	1.4757			
72	770.55	738.38	663.11		141.90	1.4836			
73	770.43	738.52	663.31		141.87	1.4948			
74	770.18	738.28	663.31		141.92	1.4919			
75	769.77	737.82	663.10		142.25	1.4824			
							141.893	1.4843	1.4873
76	766.48	734.44	652.66	0.37078	158.40	1.5492			
77	766.22	734.26	652.58		158.83	1.5498			
78	766.06	734.26	653.19		159.44	1.5446			
79	765.38	733.54	652.85		159.05	1.5415			
80	763.89	732.12	652.69		157.87	1.5218			
81	763.60	731.91	652.61		157.56	1.5244			
82	763.28	731.73	652.46		157.62	1.5341			
83	763.05	731.56	652.45		157.50	1.5310			
							158.283	1.5371	1.5400

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TABLE VI. — CO_2. SECOND SERIES. — *Continued.*

No.	p_1.	p_2.	p_3.	100 a.	t_2.	$\frac{\eta_2}{\eta_1}$.	Mean t_2.	Mean $\frac{\eta_2}{\eta_1}$.	Computed $\frac{\eta_2}{\eta_1}$.
					°		°		
84	773.83	745.39	666.15	0.37088	181.49	1.6141			
85	773.96	745.70	666.23		180.99	1.6309			
86	773.97	745.67	666.23		180.96	1.6280			
87	774.14	745.64	666.21		181.70	1.6136			
88	774.01	745.49	666.38		181.45	1.6072			
							181.32	1.6188	1.6135
89	774.41	747.71	660.30	0.37090	223.9	1.7284			
90	774.32	747.94	661.30		225.0	1.7312			
91	773.99	747.87	660.78		223.4	1.7631			
92	774.33	748.38	661.66		223.7	1.7669			
							224.0	1.7474	1.7488
93	771.47	722.92	666.03	0.37071	16.20	1.0668			
94	770.89	722.21	665.19		16.62	1.0646			
95	769.33	677.80	561.76	0.37036	17.18	1.0602			
96	769.14	677.75	561.63		17.30	1.0621			
97	768.79	677.40	561.21		17.47	1.0620			
98	768.73	677.38	561.12		17.62	1.0625			
							17.07	1.0630	1.0628

Measurements 39 to 98 furnish data for computing the constants in an empirical equation for carbonic acid, and the equation thus deduced is

$$\frac{\eta_t}{\eta_0} = 1 + 0.003725\,t - 0.00000264\,t^2 + 0.00000000417\,t^3,$$

between the limits of 0° and 224° C.

The term containing t_3 is necessary on account of the rapid curvature of the line representing the observations. The last column of Table VI. shows the values of $\frac{\eta_2}{\eta_1} = \frac{\eta_t}{\eta_0}$ deduced from this equation for the temperature means of the second column, showing as close an agreement with the observed means of $\frac{\eta_2}{\eta_1}$ as could be expected except at 100°, where the deviation amounts to about two per cent. The first series is however of much less weight than the second series. The last column of Table VI. shows the values of $\frac{\eta_2}{\eta_1}$ computed to correspond with the means of the preceding column. The average deviation of the observed means from those computed from the above equation is thus 0.0020 or about 0.15 per cent. The average deviation of the individual results from their corresponding means, taken as in the fifth series for air, is 0.0052, or about 0.4 per cent.

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Effect of Pressure.

In Series IV. for air, the total driving pressure used, $p_1 - p_3$, was varied within considerable ranges, to test whether the value obtained of $\eta_2 : \eta_1$, or of K, was thereby affected except through errors of observation. In 3, 4, and 5, $p_1 - p_3 = 248$ mm., and $\eta_2 : \eta_1 = 1.267$; in 7 and 8, under the same conditions otherwise, $p_1 - p_3 = 376$ mm., and $\eta_2 : \eta_1 = 1.266$, showing no effect due to increase of the pressure by one half. Measurements 9 to 13, made with $p_1 - p_3$ ranging from 258 to 485 mm., give values of K with an average deviation of about 0.2 per cent. Measurements 21 to 48 give values of $\eta_2 : \eta_1$ about one per cent lower than those obtained in the remainder of the series, made with greater values of $p_1 - p_3$, but the precision of these measurements is much less than of the later ones. The value of K found from 50 to 54 and 60 to 66, with $p_1 - p_3 = 530$ mm. about, is within 0.5 per cent of that found in 9 to 12, under $p_1 - p_3 = 258$ mm., and agrees precisely with 12, under $p_1 - p_3 = 361$ mm. And, finally, the mean of 97 and 98 differs from 99 by less than 0.25 per cent, though the pressures $p_1 - p_3$ are respectively 540 and 250 mm.

In the second series for carbonic acid, the effect of pressure was somewhat tested in measurements 26 to 38, where $p_1 - p_3$ varied from 370 to 111 mm. without producing any traceable effect in K. This is the best test made, owing to the greater precision of the measurements. Also in measurements 93 to 98 of the same series the pressure was changed from 105 to 207 without materially affecting the results.

In the first series for air, the average value of $p_1 - p_3$ was about 740 mm., and the mean value of $\eta_2 : \eta_1$ at $t_2 = 100°$ is 1.270, while that of the fourth series, under $p_1 - p_3 =$ from 248 to 540, is about 1.267, and that of the fifth series, under $p_1 - p_3 = 225$ mm., is 1.272, thus showing no effect traceable to the difference of the driving pressures used.

Deduction from Results.

The results of my measurements seem to show conclusively, that the variation of the viscosity with the temperature of the gas, in the case at least of dry carbonic acid and of dry air freed from carbonic acid, which may be taken as typical gases, is not proportionate either to the square root or to any numerical power of the absolute temperature reckoned from —273° C. They point thus to the inference that all hypotheses yet advanced to account for the variation of the viscosity

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of gases, and hence also for the viscosity itself, are incomplete for this phenomenon, in the same general way as are the analogous hypotheses regarding the compressibility of gases and other phenomena. The hypothetical deductions fail to accord completely with the results of quantitative measurements.

Discussion of Results of all Researches on Air and CO_2.

The experimental results which I have given in the foregoing tables, and the deduced equations, show that, unless some considerable and regular source of error affects them, the viscosity of both dry air (freed from CO_2) and carbonic acid increases with the rise of temperature according to a rate which varies with the temperature and is smaller as the temperature is higher. The ratio $\eta_t : \eta_0$ is therefore not proportional to the first power (Maxwell) of the absolute temperature; it is not expressible by a linear equation of the first degree, e. g. $\eta_t = \eta_0 (1 + b\,t)$, where $t =$ temperature C. and $b =$ a constant; nor is it given by the equation $\eta_t = \eta_0 (1 + a\,t)^n$, or its equivalent $\eta_t - \eta_0 = c\,\tau^n$, where $\tau =$ absolute temperature. The last three equations are the only ones thus far used by observers in discussing their results, although the work of E. Wiedemann and A. von Obermayer shows a decided departure from these expressions. The insufficiency of the latter equations may be shown by discussing the observational data by the logarithmic method which I used in my former paper. Nor could the equation $\eta_t = \eta_0 (1 + a\,t)^n$ be more than an empirical equation at best, unless possibly when a were expressed as a function of t and the pressure, a condition which I have not thought worth consideration at present. For the expression of my own results, I have employed merely the empirical equation with increasing powers of t, as I have found no theoretical hypothesis which led to results corresponding to the observed relation of η and t.

The deviation of both air and carbonic acid from the equation $\eta_t = \eta_0 (1 + b\,t)$ is so small, and the difficulties of precise measurement so considerable, that these deviations may often be masked by accidental errors of measurement, and by "constant errors," arising from imperfect drying or purification of the gas, from differences between the thermometer indications and the actual temperature of the gas, from faulty proportioning of apparatus, and from other sources. This discussion of my own method in these regards I give at page 25; that of others, I cannot advantageously attempt. But I

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will proceed to a review of the results obtained by all others who have worked in this field; and shall show that for air and carbonic acid no results are found giving a value of b (rate of change of $\eta_t : \eta_0$ with rise of temperature) increasing with the temperature; that some results can give only a constant value to b, owing either to the want of sufficient precision, or to the insufficient number of temperature intervals employed; that some results show a marked diminution, as do my own, of b; and that many of these last, when carefully discussed, afford material for getting at a numerical measure of the change in b which is in substantial accordance with my own results. These facts indicate, either that all measurements show conclusively that b does diminish with rise of temperature, or that the method of transpiration through capillary tubes upon which these demonstrations rest (for the measurements with oscillating plates are of insufficient precision for determination of this change) is faulty in either its experimental application or its mathematical theory. In the consideration of this last proposition the statements which I have made at page 25 should be reviewed.

In the discussion of the results of former observers, I have adopted the graphical method as best adapted to the purpose; but as the point to be considered is one in which changes in the fourth and sometimes the fifth place of significant figures must be exhibited, a special device must be resorted to. I have therefore assumed for carbonic acid an equation $\eta_t = \eta_0\left(1 + \frac{t}{300}\right)$, and for air $\eta_t = \eta_0\left(1 + \frac{t}{400}\right)$, as convenient equations to which to refer the results on these gases respectively. I have computed for two or many temperatures (usually those of observation) values of $\eta_t : \eta_0$ from these equations, and subtracting these from the experimental data for the same temperature (or from ratios $\eta_t : \eta_0$ deduced by myself from the data), I have obtained differences or residuals which I have used as ordinates in the lines shown in the plots on Plates I. and II. These lines or "residual curves"* easily show the fourth place of decimals in the ratio $\eta_t : \eta_0$, and develop as a curvature the change of the rate b. As the residual curves are plotted, convexity upwards shows a diminution of b with rise of t, concavity upwards would show an increase of b, and no curvature of course indicates a constant value of b. Above and below the 50°, 100°, and 200° points of my own results will be seen a vertical row of points marked 1 %, 2 %, —1 %, etc., which indicate dif-

* See Pickering, Physical Manipulation, i. 12; Jour. Franklin Inst., lxi. 272.

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ferences in $\eta_t : \eta_0$ of 1, 2, etc. per cent from my results, and afford a convenient means of comparing the relative concordance between the results of various observers. It should be borne in mind, however, that some of the lines are plotted from means, some from single observations, and others from equations deduced either by the observers or by myself. The individual points, therefore, must not be used without qualification as a measure of the precision of the results obtained by any single observer.

Carbonic Acid, CO_2.

The curve OA on Plate I. is from the equation deduced at page 17 for my own results. There can be no question as to the decided curvature shown being far beyond the limits of variable experimental error. My computations have also shown that the third power of the temperature in the linear equation was necessary. The experimental means are marked along the curve.

The curve DOB is from an equation of the same form

$$\eta_t = \eta_0 (1 + At + Bt^2),$$

in which A and B are computed from the results of A. von Obermayer * with capillary "I." The term Ct^3 was omitted because of the smaller number of points and their somewhat less precision. That the line represents approximately the data will be seen from noting the distribution about it of the observed points. The curvature is here also undoubted, although Obermayer merely remarks that "it follows from these experiments with some probability that the increase in coefficient of friction with rising temperature is less at higher than at lower temperatures." A comparison of this curve with mine shows that Obermayer's results and my own are in substantial agreement as to the rate of change in b, the curvature of the two lines being very nearly the same. Indeed, if my results be thrown into the same equation, using only the first and second powers of t, the value of B becomes 0.00000136, while that from Obermayer's data is $B = 0.00000137$. The value of A from my results is, however, considerably larger than from Obermayer's, so that his value of $\eta_t : \eta_0$ at 100° is about 0.7 per cent below mine, and at 200° about 1 per cent below. The line OC is from the equation

$$\eta_t = \eta_0 (1 + 0.003582\, t - 0.00000105\, t^2),$$

* A. von Obermayer, Wien. Ber., lxxiii. 468 (1876).

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deduced by me from Obermayer's experiments at the three indicated temperatures with the capillary "D." This is in still closer agreement with mine in numerical values of $\eta_t : \eta_0$, but has slightly less curvature ($B = 0.00000105$). The value for A in my results is 0.003637, with the same terms in the equation. When methods as different in detail as those of Obermayer and myself are in so close agreement as these appear to be when thus discussed, the chances of large constant errors other than those inherent in the use of transpiration methods seem to be much reduced.

On the line *JH* are three points showing the results obtained by Eilhard Wiedemann. The line is drawn from the equation

$$\eta_t = \eta_0 (1 + 0.003727\, t - 0.00000320\, t^2),$$

which I have deduced from these three points. The curvature is much greater than for either of the other lines, the value of B being more than twice as great as in the lines *OA* and *OB*, and three times as great as in *OC*. A reference to my discussion of the results for air will show that Wiedemann's results there exhibit similar relative characteristics. Up to 100° for CO_2 the results differ numerically by less than 0.7 per cent from those of Obermayer and myself, but at 200° the difference is nearly 3 per cent.

The results by Puluj, as shown by the line *OF*, obtained by oscillating plates, are smaller than all others, a difference which characterizes his results for air. The range of temperature used is too limited to render the results available in the present consideration.

Conclusion. — In the absence of any really satisfactory means of assigning proper weights to the results of Obermayer, Wiedemann, and myself, it seems best to allow the results to stand in the form above given, without an attempt to deduce a mean.

Air.

In Plate II. are shown the residual curves for all available observations on air. The line *IJ*, representing Maxwell's results, doubtless owes its steepness to some large constant error, for which several explanations have been offered. The lines for O. E. Meyer's results from capillary transpiration are

AB from Eqn. $\eta = 0.000171\ (1 + 0.0024\, t)$, Range 20° to 99°;
CD " " $\eta = 0.000170\ (1 + 0.0028\, t)$, " 21° to 100°;
EF " " $\eta = 0.000174\ (1 + 0.0030\, t)$, " 21° to 100°;

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and from oscillating plates the line is GH from the mean of the equations,

$$\eta = 0.000186\ (1 + 0.0030\ t),$$
and $$\eta = 0.000189\ (1 + 0.0025\ t),\quad \text{Range } 19^\circ \text{ to } 82^\circ,$$

given for different methods of computing one series of data. It is perhaps worthy of remark, that the mean of Meyer's results at 100° agrees with the results of my fifth series within 0.2 per cent. Meyer's observations were made chiefly at two temperatures, and thus, as well as on account of the magnitude of the errors of observation, are incapable of indicating the small deviation of $\eta_t : \eta_0$ from the equation of the first power of t.

The observations of Puluj are shown by the lines KL, MN, OP, QR, and ST, of which all but ST are from transpiration experiments, this being by oscillating plates. From the data which I have used in plotting the lines Puluj deduces the first power equations: —

KL,	$\eta = 0.000179\ (1 + 0.0024\ t)$,	Range 13°.0 to 27°.0.
MN,	$\eta = 0.000179\ (1 + 0.0023\ t)$,	" 13°.6 to 76°.7.
OP,	$\eta = 0.000181\ (1 + 0.0022\ t)$,	" 1°.1 to 77°.4.
QR,	$\eta = 0.000180\ (1 + 0.0021\ t)$,	" 1°.5 to 92°.7.
ST,	$\eta = \text{constant}\ (0.03855 + 0.00010213\ t)$	" −3°.0 to 25°.0.

From the plots on Plate II., and from others which I have made, it appears to me that the data shown in KL cannot be represented by a straight line, nor are they to be relied upon for giving the rate of change of $\eta_t : \eta_0$ at all, the curvature of the line KL which approximately represents the data being undoubtedly the result of uncorrected constant error. The points of the line MN show an upward convexity of slight amount; those of the line OP are so irregularly distributed as to conceal any slight systematic deviation from the straight line. The points of QR are also very irregularly distributed, but are unquestionably more nearly represented by the line QR, which I have drawn approximately through them, than by the straight line SR_1, which corresponds to the equation given by Puluj, or by any other straight line. The line QR should certainly be convex upwards.

The numerous experiments of Obermayer give almost unquestionable evidence that even for air the coefficient of viscosity increases at a less rapid rate at higher than at lower temperatures. The line $a\,S\,b\,c$ represents the mean of results by capillaries "11," "26," and

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"D." (I was obliged to omit "I" from consideration, owing to an apparent error. Wien. Ber., lxxiii. 440.) The separate results are fairly accordant. This line agrees quite closely with my fifth series, *SY*. The results obtained with a brass capillary are indicated by the line *d e*, which is a continuation also of *S b*, since the brass capillary agreed substantially with the others at *b*. The curvature of this line, as well as of *a S b c*, is decidedly convex upward, much more so than *SY*. Obermayer's further series with capillary "D" is of much value. It is represented in the line *g h*, and the three marked points indicate the points yielded by the experiments. This line is also decidedly convex upward, and its curvature seems to be beyond the range of variable errors of measurement. I have connected the individual points with each other by a broken line, because, owing to the small number of points, almost any form of curve could be drawn through them, and to select any one equation would be wholly arbitrary. This remark applies also to the line *UV*, representing Wiedemann's results. This line is still more convex upward than either of the preceding. The line *WX*, representing Warburg's results with oscillating plates, is in substantial accord with the results by Obermayer, Wiedemann, and myself, as well as with the mean of Meyer's results; but as it is derived from observations including but one temperature interval, it cannot serve to determine any beyond the first power variation in the coefficient.

To show the relation of the several lines to one from an equation of the exponential form which has been so generally adopted, I have drawn the line *Z* from the equation

$$\frac{\eta_t}{\eta_0} = (1 + 0.003670)^{0.76}.$$

The fifth series of my own results is shown in the line *SY*, the experimental means being denoted by crosses. The deviation of *SY* from a straight line is quite slight, and I am confident that this is a close approximation to the true result, and that the greater curvature of the lines from my own earlier results and those of other observers is due in part to impurities in the air, either in the form of carbonic acid or of vapor of water. I regard those of my measurements on air which precede the fifth series merely as checks upon the accuracy of the process, and as possessing small weight as compared with that series, for reasons assigned in the following Critique of the Method. The same is true of all but the last series with carbonic acid.

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Critique of the Method.

Since the variation to be studied in the present investigation is one of quite small amount, and is determined as the result of a somewhat complex measurement, any systematic error of even quite small magnitude might mask the quantity sought. It is essential, therefore, to show how far such errors of sensible magnitude have been avoided or eliminated. In the following pages I have given a somewhat detailed discussion of the possible sources and magnitudes of error in my measurements, and of the accuracy attained in the various component measurements.

The advantages of the method arise from its simplicity and directness. The only measurements of precision required are of the temperature of the second capillary, and of the lengths of several mercury columns. No measurements of volume are involved. The two capillaries through which identically the same masses of gas are successively transpired are as nearly as possible alike, and under the same conditions except as to temperature. The gas is transpired through each under nearly the same pressure difference, and at a pressure not far from one atmosphere. The flow of the gas is perfectly uniform, except for slight accidental fluctuations, throughout the whole of a measurement or set of measurements, tending thus to the elimination of a class of errors possible in such methods as that of oscillating plates, or of transpiration when the driving pressure falls from a given initial to a less final amount. The disturbing effect of eddies, or other special action, at the entrance to or exit from the tube, would be in part eliminated in this method, since the measurements give the ratios of the resistance in two tubes under constant and nearly identical conditions. No complete discussion of these effects has been yet given, and their experimental elimination certainly seems more easy than their mathematical treatment. It seems quite possible that they are still sensible sources of deviation from the assumed law of transpiration, but as the magnitude of the disturbance is small, and cannot be widely different in the two tubes used in this apparatus, and since the determination of the constants of the tubes dependent on their diameters, lengths, &c. are experimentally made by the same process and under conditions identical with the subsequent work, the resulting error must be small. It should be noted, also, that the debated question as to the slip of the gas over the inner surface of the glass tube has an influence in my results only to the extent by which this slip is affected by the temperature.

The freedom of the method from constant error is indicated by the close accordance of the results on dry air as obtained by the first, fourth,

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and fifth series. The first series was made with an apparatus totally different from that afterwards used in all details of disposition of parts and of instruments used, except that the tube I of that series was the same that was afterward cut into three pieces, of which two nearly equal ones served as the capillaries in the fourth and fifth series. Observations with other tubes in the preliminary measurements, however, checked satisfactorily with these. The instruments and arrangements for measuring the pressures in the fourth series were wholly different from those used in the fifth series. The results at 100° for the three series are given in the following Table VII., in which the last two values are taken from the equation deduced for the respective series.

TABLE VII.

Series.	$\frac{\eta_{100}}{\eta_0}$.	d.
I.	1.270	—0.0017
IV.	1.2672	—0.0045
V.	1.2717	0.

The quantity deduced as the result of each experiment of the present investigation is a ratio between the coefficients of viscosity of a gas at two different measured temperatures. As I have already shown,* this ratio is expressible by the following equation:

$$y = \frac{\eta_t}{\eta_0} = \frac{R_2^4 \lambda_1}{R_1^4 \lambda_2} \cdot \frac{p_2^2 - p_3^2}{p_1^2 - p_2^2} \cdot \frac{1 + 3At}{1 + at},$$

where

η_t = coefficient of viscosity of the gas at $t°$ C.
η_0 = " " " " 0° C.
R_2 = radius, and λ_2 = length, of second capillary at $t°$.
R_1 = radius, and λ_1 = length, of first " " 0°.
p_1 = pressure of gas at entrance to first capillary.
p_2 = " " exit from first capillary, which is the same as that at entrance to second.
p_3 = pressure at exit from second capillary.
t = temperature of second capillary.
0° = " first "
A = coefficient of linear expansion of the glass.
a = mean coefficient of expansion of the gas between 0° and $t°$, and under the pressure p_2.

* See references at end of paper.

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Writing for brevity,

$$\frac{R_2^4 \lambda_1}{R_1^4 \lambda_2} = K, \text{ a constant;}$$

$$\frac{p_2^2 - p_3^2}{p_1^2 - p_2^2} = \phi(p), \text{ a function of } p;$$

and

$$\frac{1 + 3At}{1 + at} = \psi(t), \text{ a function of } t;$$

there results,

$$y = K \cdot \phi(p) \cdot \psi(t).$$

Differentiating this expression successively with respect to K, p_1, p_2, p_3, t, A, and a, then substituting for dy, dK, dp_1, &c. Δy, ΔK, Δp_1, &c., and solving with respect to ΔK, Δp_1, &c., the following expressions may be obtained:

$$\Delta K = \frac{1}{\phi(p) \cdot \psi(t)} \cdot \Delta y$$

$$\Delta p_1 = -\frac{(p_1^2 - p_2^2)^2}{2p_1(p_1^2 - p_2^2)} \cdot \frac{1}{K \cdot \psi(t)} \cdot \Delta y$$

$$\Delta p_2 = \frac{(p_1^2 - p_2^2)^2}{2p_2(p_1^2 - p_3^2)} \cdot \frac{1}{K \cdot \psi(t)} \cdot \Delta y$$

$$\Delta p_3 = -\frac{p_1^2 - p_2^2}{2p_3} \cdot \frac{1}{K \cdot \psi(t)} \cdot \Delta y$$

$$\Delta t = -\frac{(1 + at)^2}{a} \cdot \frac{1}{K \cdot \phi(p)} \cdot \Delta y$$

$$\Delta A = \frac{1 + at}{3t} \cdot \frac{1}{K \cdot \phi(p)} \cdot \Delta y$$

$$\Delta a = -\frac{(1 + at)^2}{(1 + 3At)t} \cdot \frac{1}{K \cdot \phi(p)} \cdot \Delta y.$$

From these, by inserting the proper numerical quantities taken from any suitable experimental result, may be computed the numerical values of ΔK, Δp_1, &c., corresponding to any assumed value of Δy, and thus may of course be found the amount of change (or error) in K, p_1, &c., which would produce in y the assumed change (or error) Δy.

For the present purposes it is convenient to assume for Δy the same fractional value at all temperatures, and a convenient and suitable magnitude is $\Delta y = 0.001\, y$. The following Table VIII. gives the

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numerical values of ΔK, Δp, Δt, &c., deduced from the experimental data of the second series for carbonic acid. The first column gives the tabular number of the measurements from which the data were taken.

TABLE VIII. $\Delta y = 0.001\, y$.

No.	t_2.	ΔK.	Δp_1.	Δp_2.	Δp_3.	Δt.		ΔA.		Δa.		ΔH.
	°		mm.	mm.	mm.	°	per ct.		per ct.		per ct.	
50	59.6	0.00104	−0.043	+0.028	−0.074	−0.33	−.56	+0.0000057	+70	−0.000021	.57	7.6
62	100.2	0.0010	−0.037	0.025	−0.077	−0.37	−.37	0.0000033	40	−0.000014	.40	
82	157.6	0.0010	−0.031	0.023	−0.084	−0.43	−.43	0.0000021	26	−0.000010	.27	
90	225.0	0.0010	−0.026	0.020	−0.092	−0.50	−.50	0.0000015	19	−0.0000082	.22	2.5

Probable Effect on y of Instrumental Errors and Errors of Observation on the Values found and used for K, p_1, p_2, etc.

Since the accuracy in the determination of K depends upon that of p_1, p_2, and p_3, when both tubes are in ice, and thus under identical conditions, the latter quantities will be first considered.

I. Δp.

Constant errors in p_1, p_2, p_3, may be due to instrumental error of the barometer, or of the cathetometer which is used in the measurement of the mercury columns. Of course the fractional precision of the pressure measurements would be increased by increasing the driving pressure, but the possible deviation from the assumed laws of transmission of the gas through the tubes and of the increased liability to leakage with great rarefaction renders the use of a small pressure desirable. The cathetometer error has been reduced by the application of corrections determined for each decimeter of the scale by Prof. Wm. A. Rogers of Cambridge, and it was found not difficult to read the length of the mercury columns in the gauges with a probable error of less than 0.02 mm. The barometer was No. 835, made by James Green of New York, and had a scale of millimeters with vernier reading to 0.1 mm., and read by estimation as nearly to 0.01 as possible. Its instrumental error after careful refilling was determined by tests with the cathetometer and by indirect comparison with instruments of the U. S. Signal Service, and was probably under 0.3 mm., possibly considerably under that amount. As will be seen farther on, a constant error of this magnitude would have no sensible effect.

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Further constant errors may be due to the following causes:—

1. Impure mercury in gauges. Carefully redistilled mercury only was employed. Any slight error from this source would be nearly eliminated through the use of the same mercury in the determination of both y and K.

2. Imperfect drying of the gas. The gas was retained over concentrated sulphuric acid from fifteen minutes upward before being passed through the drying tubes into the apparatus. These tubes were of more than 0.5 meter in length, and of such size that their contents would supply the apparatus with gas for upwards of a quarter of an hour. They contained anhydrous phosphoric acid, of which the surface was made greater by placing a portion of it upon a horizontal partition of wire gauze. The apparatus was dried as thoroughly as possible before the beginning of each day's observations, by repeated careful exhaustions, and by the transpiration of the dried gas during several hours.

3. Leakage into the apparatus in the portion where p_1 was measured would not occur, as this pressure was always equal to or in excess of the external. Leakage into the space containing the gas under p_2 would be fatal to accuracy, and was prevented at the necessary joints by placing as close together as practicable the ends of the glass tubes to be joined, wiring the rubber tube used as a connector firmly into place, and surrounding the tube with a bath of glycerine to preserve the rubber from drying and cracking. This arrangement showed upon careful tests no indication of leakage either of air or of moisture; and it is believed that such could not have occurred in amounts sufficient to vitiate the results to any appreciable extent, in view of the other precautions taken against accumulated moisture. Leakage into the space whose pressure was p_3, unless absurdly large in amount, could not cause error.

4. More or less complete clogging of the capillary tubes which would bring about any change in diameter was not indicated either by the course of the direct experiment, or by the check measurement of K made at several times.

5. Badly shaped connecting tubes would have introduced frictional resistance of an uncertain magnitude, but the tubes used were designed of suitable size to make the velocity through them so small as to require a motive pressure certainly less than 0.01 mm.

6. There arises naturally a question as to how far the pressure at which the gases are transpired affects the viscosity, a point which is discussed further at page 18 of this paper. That this effect is not

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outside the limits of error of observation in this method is however shown by the groups of measurements of K at various pressures as given in experiments 26 to 38 on CO_2. These show that for pressures $p_1 - p_2$, as given in the subjoined table, varying from 159.7 to 54.9 mm., the mean values of K deduced differ at most by less than 0.14 per cent, and the difference is also not progressive in either direction, but irregular, the means for the extremes of pressure being precisely the same.

$p_1 - p_2$.	K.
159.7 mm.	1.0387
70.9	1.0373
61.9	1.0375
54.9	1.0386

In addition to this, the close agreement of the results of the first series on CO_2 with those of the second series afford an important check upon the latter, since the former were made with wholly different measuring and heating apparatus, and at pressures from two to three times as great.

7. It should be here noted, that any unequal action at the entrance of the various tubes which might vitiate results obtained by any direct method are to a large extent eliminated by the differential method here used, and would probably enter, if at all, as errors of the second order of magnitude; also, as elsewhere stated, that the surface friction or slip of the gas over the walls of the tube would influence the results only in so far as it changed with the temperature, and would therefore probably be imperceptible.

Variable errors may enter from instrumental sources in readings of the barometer or of the cathetometer. Errors of observation in the measurement of the length of the mercury columns by use of the cathetometer would rarely exceed 0.02 mm.; but this amount is considerably less than the pressure changes which occurred in the average experiment. The barometer reading was also obtained with a deviation of less than 0.02 mm. as far as concerns errors of observation. To eliminate as far as possible progressive changes in p_1, p_2, and p_3 during the limits of time required for making a complete set of observations at any given temperature, a pair or more of readings of each was taken, symmetrically distributed in regard to time, so that the means should correspond to about the same instant, and thus be as nearly as possible equivalent to simultaneous observations. The order of readings in the most complete sets would thus usually be barometer, thermometer giving temperature t of bath, gauges A, B, C, temperature

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t, gauges C, B, A (reversing order on ends of column also), temperature t, barometer, and finally the readings of auxiliary thermometers for temperatures of gauges, etc.

In order to eliminate as far as possible any uncertainty in setting the cross-hairs of the telescope upon the true top of the mercury meniscus, a difficulty requiring special precaution when readings to 0.01 mm. are attempted, the device was adopted of placing about the tube a clasp with a dull black internal surface. This clasp was placed upon the tube above the mercury column, and was pushed down the tube until the plane of its lower edge was nearly tangent to the mercury meniscus, which then appeared black against a bright background otherwise secured for it. Another convenient method is to make the meniscus bright against a dark background, which is accomplished readily by placing behind the tube a piece of paper separated along a horizontal line into two portions, the upper of which is white, the lower black. When a reading is to be taken, this is adjusted at such a height that the black shall be just visible above the top of the meniscus. In both of these methods it is essential that care be taken that the adjusted black edge be not more than about one fifth of a millimeter above the top of the meniscus, as otherwise error may be introduced through mistaking the reflection of the line by the meniscus for the actual top of the meniscus.

Errors in observation of the height of the barometer affect p_1, p_2, and p_3 by equal amounts in any given experiment. The effect of such errors will therefore be small, and its magnitude, given in the last column of the preceding table, may be demonstrated in the following manner. In the expression

$$y = K \cdot \frac{p_2^2 - p_3^2}{p_1^2 - p_2^2} \cdot \psi(t)$$

may be inserted $p_1 = H + c$, $p_2 = H + b$, $p_3 = H + a$, where H is the barometric reading and c, b, and a are the gauge readings, at entrance, middle, and exit of the apparatus. Thus,

$$y = K \cdot \frac{b - a}{c - b}\left(1 + \frac{a - c}{2H + c + b}\right)$$

$$\therefore \quad \frac{dy}{dH} = -K \cdot \psi(t) \cdot \frac{a - b}{b - c} \cdot \frac{2(a - c)}{(2H + b + c)^2}$$

$$\therefore \quad \Delta H = -\frac{c - b}{b - a} \cdot \frac{(2H + b + c)^2}{2(a - c)} \cdot \frac{1}{K \cdot \psi(t)} \cdot \Delta y.$$

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As shown by the number deduced from this expression and given in the table, the value of ΔH for $\Delta y = 0.1$ per cent will be at least 2 mm. throughout the range of these measurements. Also when it is considered that constant barometric errors, since they enter with nearly the same magnitude and effect, but with opposite signs, in the determinations of K and of y, become inappreciable in effect when not amounting to several millimeters. That the value of ΔH is so large will be seen, on inspection of the foregoing differential, to be due in part to the small value of the differences of initial and final pressures used in these experiments.

An inspection of measurements 26 to 38 of Table VI. will show that the average deviation in these determinations of K is 0.2 per cent. The average deviation in K which could come from the above-mentioned sources will be seen, however, to be less than 0.2, probably as small as 0.1 per cent, since K as measured is a function of p_1, p_2, and p_3 only. It thus appears probable that the assumed precision in the instrumental measurement of the pressures is not far in error.

Among other sources of variable error are: —

1. Irregular action of the aspirator causing more or less irregular changes in the amount of pressure at the exit of the gas, i. e. corresponding to p_3. Fluctuations of this sort would of course be felt at once on the gauge, but the corresponding adjustment of p_2 would require some time, as it would require the transpiration of a definite amount of gas from the p_2 space to the p_3 space. By the use of the regulator which I have devised for the purpose, and which has been already described at page 5, it has been found feasible to keep the pressure constant within a millimeter during a whole day's experimenting, while the water pressure would run from 20 to 35 pounds at frequent intervals. And, as will be seen from an inspection of the values of p_3 given in the tables, the pressure during a series of half a dozen experiments frequently remained constant within 0.2 or 0.3 mm. In a single experiment a change of 0.2 mm. was rare, the average being under 0.1 mm., including errors of reading by the cathetometer. It is thus evident, I think, that this irregularity in p_3, which is of the nature of an accidental error, since it may be of any magnitude and of either sign, would on the average introduce into y or K a deviation not exceeding 0.2 per cent, and probably less than that, and is therefore but little greater in its effect than other sources of accidental error already mentioned.

2. Owing to the want of perfect constancy in the temperature of the oil-bath, and to a slight opportunity for irregularity in the heating

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of the conducting tubes at the point of entrance to the bath, the pressure p_2 as measured at any instant might not correspond precisely with the temperature, t, observed at the same instant, since time would be required for the pressure to adjust itself by an increase or decrease of transpiration. This would, of course, slightly vitiate the result, and the amount of the effect would naturally increase with the temperature. Being a variable error, it would be partially eliminated by multiplied observations. An inspection of the records of readings giving p_2 shows that the average deviation of the pairs of readings taken in the same experiment at any given temperature increases nearly as the temperature from 0.03 mm. at 20° to about 0.1 mm. at 200° C. This in connection with the column headed Δp_2 in Table VIII. demonstrates that these observed variations in p_2 were capable of producing average variable errors in y of from 0.1 per cent to 0.5 per cent, according to the temperature.

If the average deviation of the various groups of determinations of $\eta_t : \eta_0$ in Table VI. be compared with the corresponding numbers in the table of errors, it will be seen that observed percentage deviations increase with the temperatures, while the precision required in the instrumental measurements increases much less rapidly in any case, in some cases not at all. Also the observed deviations are considerably greater than can be due to instrumental errors, including the thermometer. It seems to be thus indicated that this unequal or irregular heating is probably a correct explanation of the observed variations in p_2, and is one of the most prominent sources of error in this investigation, though at the same time one which might readily be removed by modifications of the apparatus which should lead to the maintenance of more constant temperatures of the bath, and to the elimination of any irregular heating of parts of the tube.

3. Errors in the determination of the temperatures t of the gauges would affect the values of p_1, p_2, and p_3, through the reduction to 0°. Calling 0.00018 the coefficient of absolute expansion of mercury (the cathetometer-bar expansion was separately corrected), the correction to any observed gauge reading, l, would be, of course, $C = 0.00018\ l\ t$, whence

$$\frac{dc}{dt} = 0.00018\, l, \quad \text{and} \quad \Delta t = \frac{\Delta c}{0.00018\, l}.$$

Assuming $\Delta c = 0.01$ mm., and $l = 100$ mm.,

$$\Delta t = \frac{0.01}{0.00018 \times 100} = \frac{0.01}{0.018} = 0°.55,$$

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from which it is obvious that, as the longest column of mercury read in the gauges was about 100 mm., no appreciable error would be introduced into any of these columns through errors less than 1° in their temperature measurements. With the arrangement of screens used, and taking the temperature by means of a thermometer dipping into mercury in a tube of similar dimensions and similarly exposed to the gauge tubes, no error of this magnitude could enter into t. It is also obvious that, as the gauges were placed side by side and under similar conditions in every respect, the same proportionate error would be produced in each, and this would therefore be largely eliminated. Also, for the reason given in considering the effect of barometric errors, the effect of errors in the determination of its temperature would be wholly imperceptible, and indeed all temperature correction both of the gauges and of the barometer might be omitted without seriously affecting the accuracy of the results, for the reasons already shown, and because the temperatures of the mercury columns differed but a few degrees throughout the whole research.

II. ΔK.

Constant errors in the determination of K may arise from any of the sources of error in measurement of p_1, p_2, and p_3, just discussed, which can occur under the conditions which hold during the determination of K. These conditions have already been described in detail, and it has been shown that

$$K = \frac{p_1^2 - p_2^2}{p_2^2 - p_3^2},$$

when both capillaries are at the same temperature, conveniently that of melting ice. By the method used in a previous paragraph on variable barometric errors, it may be shown that a constant error even as great as 1 cm. would have an imperceptible effect on K, and this effect would be counterbalanced and eliminated by a similar and opposite effect of this error in measurements taken with the same barometer to determine y. To a less extent the same is true of constant errors of the cathetometer scale, and it may be asserted that both of these sources of error are practically eliminated from the results of this investigation. Further sources of constant error have been sufficiently discussed in the paragraphs I. 1–7, and it should be added that, in the packing of ice about the tubes, particular care was used, not only to obtain thorough contact and surrounding at first, but to see that this was maintained.

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The *variable errors* attending the determination of K are those affecting p_1, p_2, and p_3, and already discussed; and from the measurements of Table VI. just referred to, it appears that the variable errors arise about equally from instrumental measurements and from fluctuations in p_3.

III. ΔA.

As shown by the column headed ΔA in the tables, the accuracy necessary in the value of A, the coefficient of linear expansion of glass used in the computations, increases as the temperature rises, an error of 0.1 per cent in y corresponding, however, to an error of 20 per cent in A at the highest temperature attained. The value of $3A$ used was as follows: —

At	$3A$.	At	$3A$.
0°	0.0000245	120°	0.0000266
40°	251	160°	275
80°	258	200°	284

These values were selected as corresponding quite closely to the probable change of the coefficient with change of temperature. The absolute value from 0° to 100° is based on measurements made on the same tube used, but the variation with the temperature was not measured. The error in this coefficient at 100° cannot, I think, exceed five per cent, and is not likely to reach that amount; and a consideration of the results obtained by many observers, besides those which I have myself made on similar kinds of glass, renders it certain that the value of $3A$ at 200° cannot be much more in error than at 100°. Even had a constant coefficient been employed throughout, its error introduced into A could hardly have exceeded 15 per cent at any temperature, and had this coefficient been arbitrarily assumed from the results of other observers, an error exceeding 20 per cent would have been unlikely. Since the value of ΔA in Table VIII. is 19 per cent at 225°, it appears that, with the values used, the results of the computations of y cannot have been sensibly in error from this source, even at the highest temperatures attained.

IV. Δa.

The most important quantity whose value is necessarily assumed in the computation of y is the coefficient of expansion of the gas used. This quantity and the temperature of transpiration, as may be seen from the columns headed Δa and Δt, or from the expression giving y,

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affect the value of y to an equal extent, and the two must be determined with a precision ranging from 0.57 per cent at 60° to 0.22 per cent at 225°, in order that each shall produce in y an error of less than 0.1 per cent. It is well known that the value of a for all gases changes with the pressure and temperature under which they expand. In the case in hand, the gas expands under the constant pressure p_2 from the temperature 0° of the first capillary, to that t of the second. The experiments of Regnault furnish the best data for this coefficient, and I have adopted his figures without reducing them for the corrected value of the expansion of mercury, as the small change which would be necessary would not sensibly affect my results. Regnault gives as the coefficient of expansion of carbonic acid under constant pressure

At 760 mm.	$100\,a = 0.37099$
" 2520 "	" $= 0.38455$

Although the function connecting the pressure and coefficient of expansion is unknown, yet simple extrapolation from these data gives values of a of sufficient relative precision for the present results, as the total variation of a within the range of p_2 used is only about 0.12 per cent. The values actually used are given in the tables of experimental data, so that the general effect of this correction can there be noticed, and the data are sufficiently complete to allow a recalculation with other values if desirable. It will be seen here also, as in the value of A, the change in the coefficient is so small as to produce effects of less than 0.1 per cent if neglected altogether, but the retention of both favors the elimination of accumulated systematic error in y as a function of t. For this reason, a similar precaution has been taken in the computations for air, although in that case it is even less necessary.

V. $\Delta\, t$.

The precision necessary in the measurement of t, the temperature of the second capillary, is shown in the column headed $\Delta\, t$ in Table VIII.

1. As this investigation was aiming at the determination of the change of rate of variation of the viscosity with the temperature, and as this change was known to be small, it seemed of special importance that all precautions should be taken to eliminate systematic errors. And as thermometric measurements, even when conducted with more than ordinary care, are particularly liable to such errors, especial atten-

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tion was devoted to this branch of the work. The precision obtained in the thermometry was doubtless greater than was necessary to correspond to that obtained in other parts of the determination of y, especially below 60°; but it is doubtful if a satisfactory elimination of constant errors could have been obtained with any less care.

The investigations on thermometry which I have made, and still have under way, will be discussed here only in their relation to the measurements given in this paper. The important problem of how far the mercurial thermometer is available as a convenient representative (proxy) for the air thermometer at temperatures up to 300° C., and under what conditions and methods it shall be so used, does not enter to any considerable extent into the work in hand, on account of the comparatively small degree of accuracy required in my measurements, even at the highest temperature (225°) used. The results which I have already obtained in this direction I hope to supplement by enough other material of the same nature to render the whole of sufficient value to be given by itself at some future time.

All the thermometric readings were taken with the bulb immersed in the oil-bath around the second capillary to a depth of about two inches. Above this point, the projecting stem was surrounded by a thin-walled glass tube, closed at the bottom by a rubber stopper through which the thermometer stem passed, and filled with water or glycerine, according to the temperature of the oil. This stem bath was stirred by a vertically moving stirrer, and its temperature was determined at one or more points, according to the length of the mercury column enclosed, by one or more auxiliary thermometers.

The readings were properly corrected for calibration error (except in the case of the Baudin normals, which were found by calibration to be accurate to two or three tenths of a division), for temperature of exposed stem, for true value of unit of scale (error of fixed points), and for deviation from the air thermometer. Poggendorff's correction becomes unnecessary where the mercurial thermometer, as in this work, is compared with the air thermometer direct, and all readings are reduced to that standard.

The thermometers used were respectively, one by Casella of London, No. 32378, and two by Baudin of Paris, Nos. 7335 and 7789. The following table gives the description of these, and of several others to be referred to later.

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TABLE IX.

Mark.	Approx. Length in cm.	Range.	Graduation.	Length occupied by 1° C.	Maker.	When made.	Owner.
		° °	°	cm.			
7335	46	100 to 200	0.1 C.	0.5	Baudin.	October, 1878.	S. W. Holman.
7789	40	100 to 200	0.2 C.	.....	Baudin.	.....	S. W. Holman.
32378	46	−15 to 110	0.2 C.	0.32	Casella.	Kew Register, 1873, -4, -8.	S. W. Holman.
6163	50	−6 to 40	mm.	0.9	Baudin.	1876-77.	Physical Laboratory, Johns Hopkins University.
7334	61	0 to 100	° 0.1 C.	0.5	Baudin.	October, 1878.	S. W. Holman.
Kew 104	66	−21 to 103	0.5 F.	0.46	Welch.	July, 1853.	Professor Barker, University of Pennsylvania.
Geissler	45	−3 to 102	0.1 C.	0.38	Geissler.	(?)	Chemical Laboratory, Johns Hopkins University.
368	48	About 0 to 100	Arbitrary equal volumes.	0.32	Fastré.	1851.	Professor Gibbs, Harvard College.
376	48	About 0 to 100	Arbitrary equal volumes.	0.31	Fastré.	1851.	Professor Gibbs, Harvard College.
3235	40	32 to 212	1°.0 F.	0.16	Casella.	(Quite old.)	Harvard College Observatory.

It is always somewhat unfortunate, but usually unavoidable, to have the stem of the thermometer at a temperature lower than that of the bulb, and the correction from this cause increases about as the square of the temperature of the bulb. Among the discussions of the methods of correction for this error may be cited those of Kopp, Regnault, Holtzman, and, more recently, Wüllner * and Mills.† After a careful experimental trial and consideration of these, it appeared to me that, for the present purposes, results fully equal to the requirements would be obtained by the use of a stem bath as above described.

Let s = mean temperature of this bath.

t = actual temperature of bulb (to be determined).

0.000156 = coefficient of apparent expansion of mercury in glass.

n = length of mercury column in units of the scale graduation at temperature s.

r = direct reading of thermometer corrected for calibration error.

Then

$$t = r + 0.000156\ (t - s)n,$$

or approximately

$$t = r + 0.000156\ (r - s)n,$$

* Lehrbuch der Experimental-Physik, iii. 312.

† Proc. Royal Soc. Edinburgh, xxix. 569.

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since $t = r$ very nearly. When, however, $t - r$ becomes sufficiently large, the value of t as computed by the second expression must be considered as a first approximation only, and a second or third must be computed.

Without entering into the further discussion of thermometry which I have made, a portion of which was presented in a paper (unpublished) read at the Boston Meeting of the American Association for the Advancement of Science in 1880, I will assert that the errors in my thermometric work are below the values assigned to Δt in Table VIII.

In order to determine the deviation of the mercurial thermometers used in my measurements from the air thermometer, a direct comparison was made of these and several others, the results of which possess some interest, and will be here given.

Through the kindness of Prof. H. A. Rowland, to whom I would here express my sincere thanks for his courtesy and assistance, and by an appropriation granted by the Rumford Committee of the American Academy, I was enabled to visit Baltimore in January, 1879, and to make, in co-operation with Prof. Rowland, some thermometric comparisons, using an apparatus designed by him.

The method and apparatus for comparisons at temperatures below 100° C. were those described and discussed in full by Prof. Rowland in his valuable memoir on the Mechanical Equivalent of Heat.* It is unnecessary to reproduce the description here further than to say that a water bath was used in the apparatus, that the whole thermometer was immersed, and that in the discussion of the accuracy of the apparatus Prof. Rowland writes, † "From this table it would seem that there should be no difficulty in determining the 40° point on the air thermometer to at least 1 in 2000; and experience has justified this result." It is quite possible, however, that the result obtained in my comparison was not of quite as high precision as this, but it did not fall far short.

On two successive days a group of four thermometers was compared with the air thermometer, with the results shown in the two following tables. Thermometer Baudin 6163, whose error had already been carefully studied by Prof. Rowland, was included in both series. Table IX., on page 38, gives the complete description of the various instruments. Casella 32378 was used in my measurements below 100°. It is a fairly good instrument, but decidedly inferior to any of

* These Proceedings, June, 1879, vol. xv. pp. 77 *et seq.*

† Ibid., p. 99.

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the Baudin thermometers, both from its quite considerable calibration error, which is irregular between the 95° and 100° points, and from the lack of the calibration chamber at the top, as well as from the general form of the tube and bulb. The Kew register was also obtained, but was not used, as it was given only to 0°.1, i. e. half-divisions of the scale, and corresponds neither with the result of the comparison between Kew Standard No. 104, as given below, with the ascertained calibration error, nor with the air thermometer error. The pair of Fastré tubes, kindly lent for the comparison by Dr. Wolcott Gibbs of Harvard University, were of special interest, as being probably nearly identical with the crystal glass used by Regnault and calibrated by the method employed by him, Fastré being the maker of many of Regnault's thermometers.

The chief special points of interest in the results of these comparisons are indicated by Prof. Rowland at the place cited, and I will allude here only to the fact that all of the mercurial thermometers used in this study appear to read higher than the air thermometer below 100°.

TABLE X.

Air Thermometer.	Original Readings.					Reduced Readings.				
	6163 Baudin.	7334 Baudin.	Kew Standard No. 104.	32378 Casella.	Geissler.	6163 Reduced to Air Thermometer.	7334. Baudin.	Kew Standard No. 104	32378 Casella.	Geissler.
°						°	°	°	°	°
0.	*58.83	—0.11	32.68	+0.20	+0.69	0.	0.	0.	0.	0.
†0.43	63.5	....	33.60	0.71	....	0.52	....	0.52	0.51	....
6.08	113.0	....	43.65	6.33	....	6.08	....	6.11	6.13	....
12.68	171.55	12.59	55.47	12.91	13.42	12.65	12.73	12.68	12.70	12.82
20.49	242.0	20.48	69.55	20.77	21.29	20.49	20.63	20.57	20.56	20.74
24.55	278.8	24.50	76.90	24.80	25.33	24.54	24.66	24.61	24.59	24.81
29.51	323.9	29.49	85.88	29.80	30.32	29.52	29.66	29.61	29.58	29.83
39.45	413.1	39.43	103.72	39.76	40.22	39.47	39.62	39.53	39.54	39.80
39.15	410.7	39.15	103.23	39.48	39.98	39.20	39.34	39.26	39.26	39.56
51.17	....	51.10	124.84	51.49	51.83	....	51.32	51.29	51.26	51.49
61.12	....	61.05	142.73	61.47	61.69	....	61.29	61.24	61.23	61.41
70.74	....	70.57	159.87	71.00	71.14	....	70.83	70.78	70.76	70.92
80.09	....	79.74	176.50	80.31	80.25	....	80.02	80.04	80.06	80.10
80.39	....	80.15	177.23	80.74	80.66	....	80.43	80.44	80.49	80.51
89.95	....	89.63	194.35	90.22	90.11	....	89.93	89.97	89.97	90.03
89.92	....	89.59	194.22	90.18	90.06	....	89.89	89.90	89.93	89.98
100.00	....	99.69	212.37	100.06	99.32	....	100.00	100.00	100.00	100.00

* The original readings in ice were 58.68 and 58.45, to which .15 was added to allow for pressure of water in the comparator. This, of course, gives the same final result as if .15 were subtracted from each of the other temperatures. No correction was made to the others.

† Probably some error of reading.

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TABLE XI.

Air Thermometer.	Original Readings.					Reduced Readings.				
	6163 Baudin.	376 Fastré.	7316 Baudin.	368 Fastré.	3235 Casella.	6163 Reduced to Air Thermometer.	376 Fastré.	7316 Baudin.	368 Fastré.	3235 Casella.
°						°	°	°	°	°
0.	*58.60	111.3	—0.23	87.6	32.80	0.	0.	0.	0.	0.
3.67	90.7	130.0	....	106.25	39.35	3.61	3.64	....	3.64	3.65
11.55	161.6	170.9	11.40	147.2	53.79	11.56	11.60	11.64	11.62	11.63
20.72	243.7	217.9	20.59	194.2	70.15	20.70	20.75	20.84	20.80	20.79
32.19	347.4	276.9	32.09	253.2	90.80	32.17	32.24	32.34	32.28	32.29
39.36	411.85	313.85	39.26	290.1	103.68	39.36	39.43	39.52	39.48	39.45
50.71	....	372.0	50.57	348.2	123.65	....	50.75	50.84	50.80	50.57
60.10	....	420.0	59.92	396.45	140.80	....	60.10	60.19	60.21	60.12
73.82	....	490.6	73.59	466.85	165.68	....	73.84	73.87	73.93	73.97
86.50	....	555.25	86.16	531.22	188.20	....	86.48	86.51	86.56	86.56
....	....	550.2	85.21	525.95	186.42	....	85.45	85.50	85.45	85.51
100.00	....	624.93	99.70	600.58	212.45	....	100.00	100.00	100.00	100.00

The comparisons above 100° were of rather more importance than those below for the purpose of the present investigation. For this work the newly constructed apparatus designed by Prof. Rowland was put in use for the first time.

It consists of a massive copper vessel of circular section, having inner dimensions of 18.5 cm. depth and 23 cm. diameter, and with walls and bottom 1.2 cm. thick. Upon the carefully turned flange which forms the upper edge of the walls is bolted a correspondingly heavy circular copper plate, a projection from which enters a short distance into the vessel. From the middle of this plate, and cast upon it, rises a heavy copper bar of 10 cm. by 6 cm. cross-section outside, and 55 cm. high, but containing a vertical channel in its broader front face having a depth of 3.5 cm. and a width of 8 cm. Sheet-iron covers of suitable length and about 4 cm. width are provided to close those portions of the front of this channel which should be closed during the work. The cylindrical vessel up to the flanges is placed within a sheet-iron casing, from which rises at the back a sheet-iron outlet pipe which extends upward along the back of the channelled bar to its top. The heated gases escaping through this flue from the Bunsen burner placed beneath the copper vessel heat the bar to any desired temperature, regulation being had by means of inlet valves admitting cool air at the base of the flue.

* See note to preceding table.

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The bulb of the air thermometer is introduced into the middle of the copper vessel, and is surrounded by oil, which completely fills the vessel. The stem of the thermometer passes through a groove provided in the upper surface of the vessel. The mercurial thermometers are placed against the back of the vertical channel, with their bulbs projecting into the oil-bath to the level of the air thermometer bulb. The unoccupied space in the channel between the stems of the thermometers and the sheet iron front is filled with cotton wool or other similar substance, which may be removed at suitable points to take readings. Auxiliary thermometers are placed with the bulbs at various suitable heights along the stems of the other thermometers, and by means of them the temperature of the vertical bar, and thus of the thermometer stems, is maintained at a known temperature very nearly the same as that of the bath, so that the stem exposure correction becomes small and determinate. The massiveness and correspondingly high conductivity and calorific capacity of the whole vessel render it possible to maintain the temperature nearly uniform and constant during the time necessary for the thermometers to acquire the temperature of the bath and the readings to be taken. The oil-bath is thoroughly stirred by a sheet-iron stirrer moving vertically.

The air thermometer used was an imported instrument of the form described by Jolly.* The glass of the bulb was supposed to be of the kind used by him, and the coefficient of expansion used in my computations was based on that which he has given, and was assumed, with sufficient accuracy for the present purposes, to be, —

$t°$	Mean coeff. from 0° to $t°$.
100	0.0000278
140	286
180	295
200	300
250	31
300	32

The mercurial columns were read by means of black hard-rubber clasps sliding upon the tubes, the scale being upon the surface of a glass mirror. Readings were taken to tenths of a millimeter. For the temperature reductions of the mercury columns it was assumed that the coefficient of apparent expansion of the glass scale was

$$\Delta = 0.000181 - 0.000009 = 0.000172,$$

* Pogg. Ann. Jubelband (1874); Amer. Jour. Sci., vi. 591.

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and that the scale was correct at 0° C., which was certainly quite nearly true. The value of the coefficient of expansion of air found with this apparatus was $\alpha = 0.003679$.

In February, 1879, I made a comparison of four thermometers, including Baudin 7335 and 6161, and two other thermometers of little value, at temperatures from 100° to 250° C., with the apparatus just described. The results were fairly good, but not entirely satisfactory. Later in the same year, Dr. E. H. Hall (then a student at Baltimore) made a similar series of comparisons, using Baudin thermometers Nos. 6161, 7315, 7325, and 7324. His results with No. 6161 differed somewhat from mine, owing chiefly to the progressive change in zero which attended this thermometer during my own use of it, as well as to something of the same change during his own measurements. The results as a whole agree fairly well, and I have deemed it best to average the corrections found on all the Baudin instruments of both series, and to use this average result as a correction to Baudin 7335, which I employed in my subsequent measurements. This seemed to me the safest course, because of the general agreement of all the Baudin thermometers used, and because more comparisons of 7335 could not be made at that time to eliminate the errors entering into a single series. That the table of errors thus obtained and given below is not all that might be desired is obvious, but I am disposed to believe that at 200° it is not in error by an amount exceeding 0°.5, and by a less amount at lower temperatures, thus introducing into y an error not exceeding 0.1 or 0.2 per cent.

TABLE XII.

DEVIATION OF BAUDIN NO. 7335 FROM AIR THERMOMETER.

At °	Δ °	At °	Δ °
100	0.0	160	1.45
120	— 0.5	180	1.65
140	— 1.0	200	1.50

The measurements made at 225° were taken with Baudin No. 7789, and the correction to be applied to it was ascertained, by a comparison with No. 7335, to be +0°.8.

I have devised and had constructed an apparatus for air-thermometer corrections at high temperatures, and had hoped to be able to make a further series of comparisons of all thermometers used, but for reasons elsewhere stated the work is unfinished, and has no prospect of immediate completion.

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2. It remains to point out that, as the heating bulbs $g\,g$ and $h\,h$ were of sufficient volume to hold as much gas as would be transpired by the capillaries in a quarter to half an hour, so that the passage of the gas through them was extremely slow, as the bath around them, whether of ice or oil, was so arranged or stirred as to insure satisfactory contact with the bulbs, and as proper precautions were taken as to the position of the thermometer, the temperatures given by the latter must have been very close to the actual temperature of the gas.

By the foregoing discussion it has, I think, been shown, that the sources of constant error are unlikely to produce accumulated errors in y exceeding 0.5 per cent at the highest temperatures used, and less at lower temperatures. I am disposed to believe that in the case of air these errors are smaller than for carbonic acid.

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II.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXI.—COMPARISON OF ALCOHOL THERMOMETERS BAUDIN 8208 AND 8209 WITH THE AIR THERMOMETER AT LOW TEMPERATURES.

BY ANTHONY C. WHITE.

Communicated by S. W. HOLMAN, June 10, 1885.

THE results given in this paper were reached in a somewhat careful study of the alcohol thermometer made in the Physical Laboratory of the Institute of Technology during 1881–82. The study, though by no means exhaustive, developed some points of value which are here given. The comparison with the air thermometer agrees substantially with that published by Jolly.*

The alcohol thermometers used were two centigrade tubes, made by Baudin, Paris, in 1880. They were precisely similar, and of the following dimensions: total length, 50 cm.; length of bulb, 4.5 cm.; length of 1° C., 0.28 cm.; divided to 0°.1 C.; range from +35° to —90° C.

The air thermometer was of the Jolly type, but the mercurial columns were read by a cathetometer. Its bulb was of small size, diameter 3.48 cm., to insure a rapid equalization of the temperature within and without, and to allow the use of a small bath of liquid nitrous oxide.

The cathetometer was by Staudinger. Its scale was in millimeters with vernier reading directly to $\frac{1}{20}$ mm. and by estimation to 0.01 mm. The scale errors had been determined by Prof. William A. Rogers of Harvard University, and corrections were applied. The barometer, by James Green, was of the Fortin type, and read to 0.002 inch. The scale and instrument errors had been previously determined.

* Pogg. Ann. Jubelband (1874).

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The temperatures, T, by the air thermometer, were computed as described in Professor Rowland's paper on the Mechanical Equivalent of Heat.* The numerical value of v was 0.80 cc.; of V, 20.21 cc. The themometer was first filled with air dried by calcium chloride and concentrated sulphuric acid. The coefficient of expansion of this air was then measured several times. Six independent measurements gave values of $a =$

0.003699	0.003699
3707	3702
3685	3702

Average = 0.003699

These results are sufficiently concordant in view of the small capacity of the bulb of the thermometer, but the average is nearly one per cent higher than the proper value, 0.003670. The cause of this deviation is unknown. It is possibly in part due to imperfect drying of the air. Its effect on the resulting temperature measurements will be small, however, since a and T are determined by the use of the same mass of air, and the moisture, if any were present, must have been in so small quantity as not sensibly to influence the results through condensation, etc. If the deviation be due to any undetected constant error, it will produce but little error in the temperatures obtained, since the air thermometer is used under essentially the same conditions for the determination of a and of T.

The vessel for holding the cold bath, or "freezing mixture," was composed of several concentric glass and metal vessels, the spaces between successive vessels being filled either with dry sawdust or with a freezing mixture, or with these alternating. The arrangement employed when the freezing mixture of salt and ice was used consisted of five concentric vessels. Between the outer and the second vessels was a space filled with sawdust. Between the second and third was a space of larger capacity than the former, which contained a mixture of salt and ice. Between the third and fourth vessels was another sawdust layer; and between the fourth and inner vessels, a second freezing mixture of salt and ice; while the inner vessel was filled with alcohol, in which the bulbs were immersed and which was thoroughly stirred. A suitable cover of several thicknesses of badly conducting material was provided for the whole. When the liquid nitrous oxide was used, the whole space between the third and a

* These Proceedings, June, 1879, vol. xv.

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smaller interior glass vessel was packed with sawdust, the first outer bath of salt and ice being retained. Instead, however, of filling the innermost vessel with the liquid nitrous oxide alone, the space was first filled with fine copper turnings and filings. These occupied so much of the volume as considerably to reduce the amount of the liquid N_2O required, and at the same time by their good thermal conductivity tended to maintain a uniform temperature throughout the mass without stirring. The device was found very satisfactory in operation. The liquid N_2O was obtained by the rapid discharge of a cylinder somewhat highly charged with the gas. The cylinder was one of those in which this gas is commercially distributed for use as an anæsthetic, but was more highly charged than is usual.

In the comparison of the alcohol and air thermometers, the conditions were necessarily rather unfavorable for high precision, but the arrangements adopted are believed to have given mean results correct to 0°.5 C., or (probably) less at the lowest temperatures reached, as high a degree of precision as can be relied upon with the alcohol thermometer. The difficulty and expense of using a large bath of liquid nitrous oxide precluded the total immersion of the thermometer in the bath at low temperatures, and as it was thought desirable to work under the same conditions as to stem exposure at all temperatures, the same general arrangement was used throughout. The bulb and an inch or two of the capillary were therefore the only parts of the thermometers immersed, the remainder of the stem being surrounded by a thin glass tube of about an inch in diameter, filled with water, which, when properly stirred, rendered the temperature of the stem uniform, and measurable (by an auxiliary thermometer). The two alcohol thermometers passed side by side through the same stem bath, and had their bulbs nearly in contact with each other and with the air bulb in the cold bath.

The scale of the alcohol thermometers was supposed to be normal, i. e. of lines so spaced as to separate equal volumes of the capillary, and to give approximate degrees by direct reading. It was also supposed that the spacing of the degrees was determined by the use of ice, and by comparison with a standard mercurial thermometer at one or more temperatures, probably above 0° C., or by some equivalent process, so that one degree of the scale at or near 0° C. corresponds as closely as may be with 1° C. as ordinarily defined on the mercurial thermometer, or, more precisely, with the degree as measured with the Baudin standard mercurial thermometer. It was obviously of no special interest, therefore, to study further the temperature value of

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one division of the scale, although through the failure to do so the investigation lacks completeness.

The correction for the temperature difference between the stem and bulb, i. e. the "stem exposure correction," was made through the use of the customary expression,

$$n\,(T - t)\,k,$$

where

T = the temperature of the bulb, in these measurements given by the air thermometer.
t = the temperature of the exposed stem,
n = the length expressed in degrees of the exposed alcohol column,
k = the coefficient of apparent expansion of the alcohol in the glass of the thermometer.

The value of k was measured in two ways: first, by an independent study with the alcohol bulbs in ice and the projecting stems at measured temperatures; secondly, from the results in the comparison with the air thermometer at about 0° C. These gave results in substantial agreement, but the second method was considered more reliable, and likely to aid in eliminating constant errors in the comparison since made under the same conditions, and its value of $k = 0.00091$ was adopted.

The readings of the thermometers in ice were taken at intervals, to follow the changes with age and usage, and the instruments were never raised to a temperature above that incidental to the manipulation. The zero point of 8209 rose from —0°.18 C., in October, 1880, to +0°.16 in April, 1882. The change in 8208 was probably about the same, but the data do not extend over the same time.

The following are the mean values obtained by averaging in suitable groups the eighty readings obtained in the comparison with the air thermometer.

Air Therm.	8208.	8209.	δ_8.	δ_9.	$\delta_9 - \delta_8$.
°	°	°	°	°	°
+ 0.72	+ 0.69	+ 0.69	—0.03	—0.03	0.00
— 2.06	— 2.00	— 2.00	+0.06	+0.06	0.00
— 6.86	— 6.68	— 6.63	0.18	0.23	0.05
—10.45	—10.08	—10.03	0.37	0.42	0.05
—16.37	—15.59	—15.47	0.78	0.90	0.12
—19.80	—18.80	—18.67	1.00	1.13	0.13
—87.94	—79.02	—78.46	8.92	9.48	0.56

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The first column gives the temperatures by the air thermometer, the second column the corrected readings by Baudin 8208, the third the corrected readings for 8209, the fourth the deviation of 8208 from the air thermometer, the fifth the same for 8209, and the sixth the differences between the two Baudin thermometers. In the series of eighteen comparisons which give the means corresponding to —87°.94 the average deviation of the single numbers giving the mean in the fourth or fifth columns was 0°.16.

For the sake of comparison, the figures published by Jolly are here appended.

Air Therm.	Alcohol.	δ.
°	°	°
— 6.32	— 6.21	0.11
—11.02	—10.72	0.30
—15.25	—14.41	0.84
—19.29	—18.02	1.27
—79.44	—70.72	8.72

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III.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

By Wolcott Gibbs, M. D.,
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(Continued from Vol. XVIII. p. 274.)

Communicated June 10, 1885.

PHOSPHO-VANADATES.

The existence of a compound of phosphoric and vanadic pentoxides appears to have been first recognized by Berzelius, who regarded it simply as a phosphate of vanadic oxide and ascribed to it the formula $V_2O_3 . 3 P_2O_5$, vanadium being then supposed to have the atomic weight 61.5, so that its highest oxide would have the formula V_2O_3. Berzelius describes the supposed salt as lemon-yellow, crystalline, and slowly soluble in water. By dissolving together sodic phosphate and vanadate, adding nitric acid and evaporating at a gentle heat, he obtained a colorless solution which yielded a lemon-yellow salt in large grains made up of fine crystalline needles. For this compound, which he called phosphate of sodium and vanadic acid, he gave no formula. I shall endeavor to show that phosphoric and vanadic oxides unite in various proportions to form well-defined complex inorganic acids, strictly comparable with those which contain phosphoric and molybdic or tungstic oxides.

Phospho-vanadates are formed when alkaline vanadates are heated in contact with free phosphoric acid; when solutions of an alkaline phosphate are digested with vanadic acid or an acid vanadate; and when alkaline phosphates and vanadates are mixed in presence of a free acid, the conditions being, so far as I have observed, perfectly analogous to those which determine the formation of phospho-tungstates and phospho-molybdates. Phospho-vanadates of the heavy metallic oxides are formed when the divanadates of these oxides are boiled with solutions of alkaline phosphates or with phosphoric acid, and also when

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the corresponding metallic phosphates are boiled with vanadic acid or acid vanadates. As a rule, the salts are beautifully crystalline, and have a yellow or orange-yellow color, passing in some cases to deep orange-red.

The general characters of the phospho-vanadates are as follows. The alkaline salts have a sulphur-yellow, and in some cases bright yellow color. They are crystalline and often present minute talcose shimmering scales. The relation of these salts to water is especially remarkable. A small quantity of water simply dissolves the phospho-vanadate with a yellow color; on adding more water, the solution gradually becomes orange, then orange-red, and finally deep red. Phosphoric acid is set free, and one or more new definite salts are formed, in which the proportion of the vanadic to the phosphoric oxide is largely increased. Precisely similar changes occur in the action of water upon arsenio-vanadates. When the deep red solutions are evaporated, the changes of color described occur again in the inverse order, and finally the original yellow salt is again obtained, though not always perfectly free from the higher compound. The facility with which the salts of this series are decomposed by water makes it often difficult to obtain them in a state of absolute purity, and renders the reactions with metallic salts uncertain as characteristics. When alkaline phospho-vanadates are evaporated with nitric acid, the base is in many cases entirely separated, and phospho-vanadic acid remains in solution and may separate in crystals. This separation of fixed base often takes place in presence of an excess of phosphoric acid alone. Solutions of alkaline phospho-vanadates appear to be partially reduced by dust or traces of organic matter with exceptional facility. In such cases the solutions take a more or less distinct greenish color, and phospho-vanadico-vanadates are formed. The solutions of these last salts are not very easily oxidized by bromine or nitric acid, and it is therefore advisable in preparing phospho-vanadates to avoid as much as possible the presence of reducing agents. Alkaline phospho-vanadates dissolve readily in hot solutions of acid tungstates and molybdates, forming orange or orange-red solutions, which yield in many cases beautiful crystalline phospho-vanadio-molybdates and phospho-vanadio-tungstates.

Analytical Methods. — The method usually adopted for the separation of vanadic and phosphoric oxides by means of ammonic chloride may be successfully applied to the analysis of the phospho-vanadates. A small excess of ammonia is to be added to the solution of the salt, which is then to be heated until it becomes colorless. In this manner

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we obtain a simple mixture of phosphate and metavanadate. Ammonic chloride is then to be added, and the analysis conducted in the usual manner. This method permits the separate determination of each of the pentoxides and so far offers an advantage. On the other hand, it only applies to salts with alkaline bases. It is far more convenient, and at least equally accurate, to determine the vanadium by titrition with hypermanganate under appropriate conditions. The end reaction is usually well defined in a sufficiently dilute solution. The sum of the vanadic and phosphoric oxides may be accurately determined by precipitating the solution of the two pentoxides at a boiling heat by means of mercurous nitrate, adding mercuric oxide until a small but distinct excess is present so as to perfectly neutralize the free acid, and then boiling for a few minutes. Since the ignited mass of oxides retains mercuric oxide with some tenacity, it is best, after burning off the filter with a very free access of air, to add a weighed portion of sodic tungstate and ignite until a constant weight is obtained. When the process is carefully conducted, the fused mass contains all the phosphoric oxide and all the vanadium as pentoxide. Care should be taken to oxidize the whole of the vanadium to pentoxide as more certain. Any small quantity of dioxide present is however precipitated when an excess of mercuric oxide is present. This method applies to all salts or compounds containing oxides of phosphorus and vanadium. As regards the details of the determination of vanadium by titrition with potassic hypermanganate the following points require attention.

For the reduction of vanadic pentoxide to dioxide, it is best, after adding dilute sulphuric acid, to boil with a solution of sulphurous acid and afterward to evaporate the solution nearly, at least, to dryness upon a water bath, so as to insure a perfect reduction and at the same time to expel the last traces of sulphurous oxide. Sulphydric acid gas also readily reduces the vanadic pentoxide in presence of sulphuric acid, but there is almost always a separation of free sulphur in a state of extreme subdivision. This passes readily through the filter, and the results of the titrition are not so satisfactory as when sulphurous acid is employed as the reducing agent. The solution of vanadic dioxide should be diluted till the color is pale blue, heated to about 80°–100°, and titrated hot. In the hot solution the disappearance of the hypermanganate takes place instantly, and the end reaction is much more quickly and satisfactorily attained. The actual results are precisely the same as when a cold solution is employed, as the following titritions sufficiently prove.

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I. In a cold solution of VO_2 in SO_4H_2 three successive portions of 200 cc. each required 4.62 cc., 4.64 cc., and 4.63 cc. of hypermanganate solution.

II. At 53° C. 200 cc. as before required 4.62 cc.

III. At 62° C. 200 cc. required 4.66 cc. Process rather more rapid.

IV. At 70° C. " " 4.66 cc. " " "

V. At 80° C. " " 4.65 cc. Color vanished instantly.

VI. At 100° C. " " 4.64 cc. " " "

The following analyses will show the effect of reducing by hydric sulphide, as compared with reduction by sulphurous acid. In an acid sodic vanadate: —

I. 0.0908 gr. gave 0.0406 gr. V_2O_5 = 44.67% with H_2S

II. 0.1381 gr. " 0.0607 gr. " = 43.92% "

III. 0.1540 gr. " 0.0692 gr. " = 44.90% "

IV. 0.1625 gr. " 0.0696 gr. " = 42.99% with SO_3H_2

V. 0.1532 gr. " 0.0659 gr. " = 43.01% "

When hydric sulphide is used as a reducing agent, it often happens that the filtrate on evaporation deposits more sulphur. In titrating with hypermanganate, the final color reaction must be permanent for ten to fifteen minutes at least. As usual, the amount of hypermanganate required to color an equal volume of water and dilute sulphuric acid must be determined, and the proper correction applied.

In my paper on the vanadio-molybdates I have given another method of determining vanadium based upon the fact that a ferrous salt readily reduces vanadic pentoxide in the presence of free chlorhydric acid. I have since found that this method is not new, but was proposed and tested by Otto Lindemann * some years since.

1 : 1 *Ammonic Phospho-vanadate.* — When any ammonic vanadate is dissolved with an excess of ammonic phosphate, and nitric acid is cautiously added in small quantities at a time, a deep orange-red solution is obtained, which on heating becomes colorless, but which on evaporation to a small volume yields beautiful bright yellow granular crystals. These are to be carefully washed with cold water, in which they are not very soluble. The solution has at first a fine yellow color, but on continued dilution with water passes through the changes in color which have already been described. In this salt,

* Ueber die quantitative Bestimmung des Vanadins. Inaugural Dissertation von Otto Lindemann. Jena, 1879.

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0.5582 gr. lost on ignition with WO_4Na_2 0.1017 gr. = 18.22%
0.7667 gr. " " " 0.1393 gr. = 18.17%
0.5329 gr. gave 0.0707 gr. $(NH_4)_2O$ = 13.28%
0.9753 gr. " 0.4501 gr. V_2O_5 with $KMnO_4$ = 46.15%
0.6883 gr. " 0.3174 gr. " " = 46.13%
0.1073 gr. " 0.0495 gr. " " = 46.15%

The analyses lead to the formula

$$P_2O_5 . V_2O_5 . (NH_4)_2O + aq,$$

which requires:

		Calc'd.	Mean.
P_2O_5	142	35.99	35.67
V_2O_5	182.6	46.27	46.14
$(NH_4)_2O$	52	13.17	13.28
H_2O	18	4.57	4.91
	394.6	100.00	

I have here assumed that the simplest expression of the results of the analyses represents the molecular weight. It will, I think, appear from the study of other compounds, that it is at least probable that the molecular weight is much higher. The solution of the salt is very easily reduced by dust or traces of organic matter. The solution then contains a greater or less proportion of a phospho-vanadico-vanadate. The solution of the salt has a yellow color and a very strong acid reaction, but this probably depends simply upon the decomposition which sets phosphoric acid free.

1 : 1 *Argentic Phospho-vanadate.* — A quantity of the above-described ammonium salt was dissolved with ammonic phosphate, and argentic nitrate added to the solution in excess. A sulphur-yellow crystalline precipitate was at once formed, which was digested with very dilute nitric acid so as to remove argentic phosphate, and then presented granular yellow crystals but slightly soluble in cold or hot water. The salt is readily decomposed by dilute chlorhydric acid, and then yields a yellow solution which is probably the acid of the series. In the silver salt,

1.4134 gr. gave 0.9192 gr. AgCl = 52.59% Ag_2O
1.6267 gr. " 0.7938 gr. metallic silver = 52.41% "
1.3696 gr. " 0.2851 gr. V_2O_5 = 20.82%
1.0193 gr. lost on ignition 0.1067 gr. = 10.47%

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The analyses lead to the formula

$$P_2O_5 . V_2O_5 . 2\,Ag_2O + 5\,aq,$$

which requires:

		Calc'd.	Found.	
P_2O_5	142	16.19	16.21	
V_2O_5	182.6	20.83	20.82	
$2\,Ag_2O$	464	52.70	52.59	52.41
$5\,H_2O$	90	10.28	10.47	
	478.6	100.00		

6 : 4 *Potassic Phospho-vanadate.* — When ammonio-magnesic phosphate, $P_2O_8Mg_2(NH_4)_2$, is boiled with a strong solution of potassic divanadate, the phosphate disappears and is replaced by yellow granular masses, which are but slightly soluble in water. In this salt, after washing with cold water,

0.5401 gr. gave 0.3852 gr. P_2O_5 and V_2O_5 = 71.31%
0.3790 gr. " 0.1777 gr. V_2O_5 with $KMnO_4$ = 46.89%
0.3790 gr. lost on iguition (alone) 0.0619 gr. = 16.31%

The analyses lead to the formula

$$4\,P_2O_5 . 6\,V_2O_5 . 3\,K_2O + 21\,aq,$$

which requires:

		Calc'd.		Found.	
$4\,P_2O_5$	568	24.41	71.59	24.42	71.31
$6\,V_2O_5$	1098	47.18		46.89	
$3\,K_2O$	283	12.16	28.41	12.38	28.69
$21\,H_2O$	378	16.25		16.31	
	2327	100.00			

No magnesium and no ammonium could be detected in the salt, and it seems at least probable that the salts of the series might be prepared by the same process, other acid vanadates being substituted for the potassic salt employed. A strong solution in cold water gave a brick-red fine granular precipitate with argentic nitrate, and yellow flocky precipitates with mercurous and thallous nitrates. The mercurous precipitate was distinctly seen to contain two different compounds, and it is therefore probable that the potassic salt was decomposed even by a small quantity of cold water.

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7 : 6 *Hydric Phospho-vanadate.* — When a solution of phosphoric acid is mixed with a strong solution of sodic divanadate, a yellow uncrystalline mass is formed. This after standing some days becomes distinctly crystalline, and may be washed with cold water until the washings become orange-red. In a preparation of this salt, dried as usual upon woollen paper,

1.2172 gr. gave 0.4846 gr. V_2O_5 $= 39.81\%$
0.8553 gr. " 0.6487 gr. mixed oxides $= 75.84\%$ $P_2O_5 + V_2O_5$
0.6127 gr. lost with WO_4Na_2 0.1470 gr. $= 24.00\%$ water.

The analyses show that the compound analyzed contained no soda, and that it is a 7 : 6 phospho-vanadic acid, the formula of which may be written

$$7\ P_2O_5 . 6\ V_2O_5 . 3\ H_2O + 34\ aq.$$

The formula requires :

		Calc'd.		Found.	
$7\ P_2O_5$	994	39.76	75.83	39.81	75.84
$6\ V_2O_5$	1096	36.07		36.03	
$37\ H_2O$	666	24.17		24.00	
	2756	100.00			

The sum of the phosphoric and vanadic oxides found by difference is 76.00. After all saline matters are washed out, the acid dissolves readily in water, and gives an orange solution, which changes color on dilution in the manner already explained. I shall, after describing the phospho-vanadico-vanadates and arsenio-vanadico-vanadates, return to this and the preceding compounds.

20 : 1 *Phospho-vanadic Acid.* — When a solution of phosphoric acid is mixed with one of ammonic metavanadate, the liquid becomes orange, but after heating for a time upon a water-bath lemon-yellow, and then deposits a large quantity of a lemon-yellow crystalline salt. More of this salt is deposited on evaporating the mother liquor, and again after partially neutralizing with ammonia. The yellow salt may be drained with the filter-pump and then washed with a small quantity of cold water. The salt presents fine yellow crystals which dissolve in a small quantity of hot water. The liquid is at first yellow, but on adding more hot water, and especially on heating, it becomes orange; with more water, orange-red, and finally deep garnet-red with a very strong acid reaction. If this solution is evaporated upon a water-bath the changes of color occur in the inverse order; that is to say, the liquid

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gradually becomes orange-red, orange, and yellow, and the original salt is finally deposited. The changes of color observed are due to the decomposition of the ammonium salt by water, and the formation of ammonic phosphates and of phospho-vanadates differing in constitution from the original compound and containing a greater proportion of vanadic pentoxide for one molecule of phosphoric oxide. Phosphoric acid is also set free in the reaction. The deep red solution, on standing, deposits beautiful small granular ruby or garnet-red crystals. Of these crystals,

{ 0.3156 gr. lost on ignition (alone) 0.0691 gr. = 21.89%
{ 0.3156 gr. gave with $KMnO_4$ 0.2377 gr. = 75.32%

The analyses correspond with the formula

$$20\ V_2O_5\ .\ P_2O_5\ .\ 6\ H_2O + 53\ aq,$$

which requires:

		Calc'd.	Found.
$20\ V_2O_5$	3660	75.24	75.32
P_2O_5	142	2.92	2.79
$59\ H_2O$	1062	21.84	21.89
	4864	100.00	

The phosphoric oxide was determined by the difference. The solution of the acid has a dark red color and a strongly acid reaction. It gives cinnamon-colored flocky precipitates with nitrates of silver and thallium. The silver salt is readily decomposed by potassic chloride in presence of a trace of chlorhydric acid, giving a red solution which deposits beautiful square thin tabular crystals, the red color of which is so deep that they appear black by reflected light. In preparing the salts of this series it will probably be best to saturate a small proportion of the acid with an alkaline base, and then to add the rest of the acid. For the present the basicity of the acid is undetermined, and the assumption that it contains six molecules of water is merely provisional. It also appears probable that salts of this and similar higher series may be prepared by mixing solutions of alkaline metavanadates with those of alkaline phosphates in definite proportions, and then adding dilute sulphuric acid in small portions at a time, stirring or shaking after each addition of acid. The precise quantity of acid to be added should be calculated beforehand, which may of course be easily done if we assume a definite basicity, as, for instance, that each molecule of salt shall contain three molecules of fixed base.

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PHOSPHO-DIVANADATES.

The salts of this series are formed under conditions which have already been pointed out. They have frequently, at least, a fine yellow color, and are decomposed by water with formation of salts of other series.

Phospho-divanadate of Ammonium. — This is the yellow crystalline salt referred to as formed by the action of phosphoric acid upon ammonic metavanadate. The salt dissolves in a small quantity of cold water without apparent decomposition, but the reactions of the solution are at best rather uncertain. Argentic nitrate gives a fine bright yellow crystalline precipitate. In the ammonium salt,

1.1259 gr. lost on ignition 0.2876 gr. = 25.54% NH_3 and H_2O
1.0600 gr. " " with WO_4Na_2 0.2723 gr. = 25.69%
1.0624 gr. gave 0.1676 gr. NH_4Cl = 7.67% $(NH_4)_2O$
1.4112 gr. " 0.7534 gr. V_2O_5 = 53.40%

The analyses lead to the formula

$$P_2O_5 \cdot 2\,V_2O_5 \cdot (NH_4)_2O \cdot 2\,H_2O + 5\,aq,$$

which requires:

		Calc'd.	Found.
P_2O_5	142	20.74	20.98 (diff.)
$2\,V_2O_5$	365	53.28	53.40
$(NH_4)_2O$	52	7.59	7.67
$7\,H_2O$	126	18.39	17.95
	685	100.00	

The formula given corresponds to the provisional assumption of three molecules of water in the acid.

ARSENIO-VANADATES.

These salts are formed under precisely the same conditions as those which determine the formation of phospho-vanadates. The general characters of the salts are almost precisely similar. Like the phosphorus compounds, they are yellow or orange-yellow and crystalline. They are decomposed by water, and yield deep orange-red salts of new series, in which the proportion of vanadic to phosphoric oxide is largely increased.

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Analytical Methods. — Arsenic is most conveniently determined in these salts by reduction with sulphurous acid and precipitation of arsenious sulphide by sulphydric acid. The sulphide is then to be weighed upon an asbestos filter. In the filtrate which contains the vanadium as dioxide the vanadic pentoxide may be determined by potassic hypermanganate. Dilute sulphuric acid is to be added in place of chlorhydric acid before precipitation with sulphydric acid. Water cannot be accurately determined in these salts by ignition with sodic tungstate, as a greater or less quantity of arsenic oxide is always volatilized. The best method consists in cautiously heating the salt over a radiating cup of sheet-iron until a constant weight is obtained.

5 : 8 *Arsenio-vanadic Acid.* — When sodic divanadate and arsenate are dissolved together in boiling water, and nitric acid is added in small portions at a time, a deep orange liquid is obtained which on evaporation to dryness upon a water-bath yields an orange-yellow crystalline mass. This is to be purified by careful washing with cold water, when a beautiful crystalline orange-colored salt remains. The salt is somewhat soluble in cold, and readily in hot water. The solution is very easily reduced by dust or other organic matters, and becomes greenish-orange with formation of a greater or less quantity of an arsenio-vanadico-vanadate. It is then difficult to reoxidize the solution so as to obtain the original compound. On analysis,

0.8558 gr. gave 0.3374 gr. As_2S_3 = 36.87 % As_2O_5
0.8558 gr. " 0.4058 gr. V_2O_5 with $KMnO_4$ = 47.41 %
0.8715 gr. lost over a radiator 0.1358 gr. = 15.58 %

The analyses correspond to the formula

$$5\ As_2O_5 . 8\ V_2O_5 . 3\ H_2O + 24\ aq,$$

which requires:

		Calc'd.		Found.	
5 As_2O_5	1150	47.18	84.31	47.41	84.28
8 V_2O_5	1461	37.13		36.87	
27 H_2O	486	15.69		15.58	
	3097	100.00		99.86	

The water, as estimated by difference, amounts to 15.72, so that the direct determination is nearly correct, and no fixed base is present. In a second preparation, in which I employed residues containing arsenic and vanadium from the preparation of the arsenio-vanadico-vanadates

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to be described and oxidized with nitric acid and potassic hypermanganate, I found the ratio of the arsenic to the vanadic oxide to be as 7 : 6.

$$\begin{cases} 1.2105 \text{ gr. gave } 0.5825 \text{ gr. } As_2S_3 = 44.99\% \ As_2O_5 \\ 1.2105 \text{ gr. } \text{“ } \ 0.3748 \text{ gr. } V_2O_5 = 30.97\% \end{cases}$$

The difference here cannot be taken as water, as some manganous oxide was present; but the acid may, like the corresponding phosphorus compound, be regarded as

$$7\ As_2O_5 . 6\ V_2O_5 . 3\ H_2O.$$

Since the publication of the preliminary notice in which I announced the discovery of this class of compounds,* and threw the whole subject open to chemists, a short paper has appeared by F. Fernandez,† in which the writer describes an arsenio-vanadate of ammonium, which, except so far as water of crystallization is concerned, corresponds to the ammonic phospho-vanadate which I have described, so that we now have

$$P_2O_5 . V_2O_5 . (NH_4)_2O + aq,$$
$$As_2O_5 . V_2O_5 . (NH_4)_2O + 11\ aq.$$

Want of material has prevented a more complete study of the subject on my own part.

PHOSPHO-VANADICO-VANADATES.

The salts of this series are very readily formed by boiling an excess of a mixture of vanadic dioxide and pentoxide with alkaline phosphates, when the mixed oxides dissolve to form red or greenish-red solutions, which on cooling yield in many instances very beautiful crystalline salts. The same result is obtained by fusing the mixture of oxides obtained by igniting ammonic metavanadate with alkaline phosphates; by partially reducing phospho-vanadates, or by adding solutions of vanadic dioxide to solutions of phospho-vanadates. The alkaline phospho-vanadico-vanadates are often very beautiful, and present extremely well-defined crystals. They have usually a green color, which may be so deep as to appear black in large crystals. By oxidation they pass into phospho-vanadates.

* American Chemical Journal, iv. 577.

† Berichte der Deutschen Chem. Gesellschaft, xvii. 1632. July, 1884.

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Analytical Methods. — These are the same as those described for the analysis of phospho-vanadates. The vanadic dioxide may be determined directly by titrition with potassic hypermanganate in dilute solutions containing free sulphuric acid. In another portion of the solutions the vanadic pentoxide is to be reduced with sulphurous acid, and then determined by titrition. The whole quantity of oxides may be found by mercurous nitrate and mercuric oxide after completely oxidizing the vanadic dioxide with nitric acid.

18 : 1 : 2 *Phospho-vanadico-vanadates of Ammonium.* — When a solution of phospho-vanadate of ammonium is mixed with one of vanadic dioxide in chlorhydric acid, and the liquid is allowed to stand for some time, beautiful deep green prismatic crystals are deposited. These dissolve in hot water to a very deep red solution, and appear to be decomposed exactly in the manner which has been explained in the case of the phospho-vanadates. Of this salt,

0.3647 gr. lost on ignition with WO_4Na_2 0.0938 gr. = 25.72%
0.5318 gr. gave 0.3657 gr. V_2O_5 and P_2O_5 = 68.76%
0.4958 gr. " 0.0084 gr. VO_2 with $KMnO_4$ = 1.68%
0.4958 gr. " 0.0083 gr. VO_2 with iodine and CO_3NaH = 1.69%
0.4284 gr. " 0.0325 gr. $(NH_4)_2O$ = 7.59%

The vanadic dioxide was oxidized with nitric acid before precipitation with mercurous nitrate and mercuric oxide. The resulting percentage is to be corrected accordingly. The analyses correspond fairly well with the formula

$$18\ V_2O_5 . VO_2 . 2\ P_2O_5 . 7\ (NH_4)_2O + 50\ aq,$$

which requires :

		Calc'd	Found.
18 V_2O_5	3294	66.88	67.08
VO_2	83	1.69	1.68 1.74
2 P_2O_5	284	5.77	5.51
7 $(NH_4)_2O$	364	7.39	7.59
50 H_2O	900	18.27	18.13
	4925	100.00	

The phosphoric oxide is determined by difference only. The compound may also be regarded as a double salt ; as, for instance,

$$6\ V_2O_5 . VO_2 . 3\ (NH_4)_2O +$$
$$2\ \{6\ V_2O_5 . P_2O_5 . 2\ (NH_4)_2O . H_2O\} + 48\ aq ;$$

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but we have at present no data for deciding the question. The solution in cold water gives brown flocky precipitates with salts of silver and thallium and with mercurous nitrate, none with baric chloride at first, but after a short time the mixture becomes turbid and then deposits distinct orange crystals mixed with a brown flocky matter. The salt is therefore probably decomposed by solution.

4 : 5 : 1 *Phospho-vanadico-vanadate of Sodium.* — A boiling solution of sodic orthophosphate dissolves the mixture of vanadic oxides obtained by igniting ammonic metavanadate, and gives a greenish liquid which on cooling deposits green crystalline scales with a talcose lustre. The same salt is formed by fusing together the mixed oxides and sodic phosphate, but is in this way more difficult to obtain in a state of purity. The compound is insoluble in water, and cannot therefore be purified by recrystallization. Of this salt,

1.4264 gr. lost on ignition 0.3904 gr. = 27.37% water
1.2893 gr. gave 0.8136 gr. $V_2O_5 + P_2O_5$ = 63.10%
1.7149 gr. " 0.5815 gr. V_2O_5 by titrition with $KMnO_4$ = 33.90%
1.4190 gr. " 33.67% and 33.75%

The analyses correspond tolerably well with the formula

$$5\ P_2O_5 \cdot 4\ V_2O_5 \cdot VO_2 \cdot 4\ Na_2O + 37\ aq,$$

which requires :

		Calc'd.	Found.	
$5\ P_2O_5$	710	29.11	29.15	29.32 (diff.)
$4\ V_2O_5$	732	30.01	30.66	
VO_2	83	3.40	3.11	
$4\ Na_2O$	248	10.17	9.74	
$37\ H_2O$	666	27.31	27.17	
	2439	100.00		

12 : 12 : 6 *Potassic Phospho-vanadico-vanadate.* — When solutions of potassic divanadate and potassic orthophosphate, PO_4K_2H, are heated together, the phosphate being in large excess, a colorless solution is formed. A solution of vanadic dioxide in a large excess of chlorhydric acid then often produces almost immediately a precipitate of black granular crystals. In some cases, however, the black salt is formed only after standing some hours. Under the microscope the black crystals appear to be cubes, though this is rather uncertain. The true color is deep green. The salt is insoluble in water contain-

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ing other saline bodies; but as soon as the crystals are completely washed, they dissolve readily in hot water with decomposition, a beautiful green salt crystallizing from the solution on standing. Of the black crystals,

0.4978 gr. lost with WO_4Na_2 0.0716 gr. = 14.38 H_2O
0.1622 gr. gave with $KMnO_4$ 0.03177 gr. VO_2 = 19.59%
0.1201 gr. " " 0.02384 gr. " = 19.84%
0.1383 gr. " " 0.06032 gr. V_2O_5 = 43.62%
0.1360 gr. " " 0.05892 gr. " = 43.32%
0.5646 gr. gave 0.3035 gr. $P_2O_7Mg_2$ = 34.38% P_2O_5
0.7186 gr. " 0.3876 gr. " = 34.49% "

The analyses lead to the formula

$$12\ P_2O_5 . 12\ VO_2 . 6\ V_2O_5 . 5\ K_2O + 40\ aq,$$

which requires:

		Calc'd.	Found.	
12 P_2O_5	1704	34.14	34.38	34.49
12 VO_2	999	20.02	19.84	19.59
6 V_2O_5	1096	21.96	22.02	22.72
5 K_2O	472	9.46	9.11	
40 H_2O	720	14.42	14.38	
	4991	100.00		

The sum of the three oxides $P_2O_5 + VO_2 + V_2O_5 = 76.12$, as calculated from the formula, and 76.51 as found from the mean of all the analyses. The analyses are very difficult, partly because no perfectly satisfactory method of separating phosphoric oxide from the other oxides has yet been found, and partly because in titrating vanadic dioxide by potassic hypermanganate the end reaction varies with the quantity of phosphoric oxide present. It is true that this variation is usually within narrow limits, but it is sometimes sufficient to affect the result by as much as 0.50%.

The beautiful crystalline green salt which is formed when the black salt above described is dissolved in hot water was also analyzed.

0.5918 gr. gave 0.3771 gr. $PtCl_6K_2$ = 12.37% K_2O
0.4766 gr. lost with WO_4Na_2 0.0718 gr. = 15.06%
0.1617 gr. gave with $KMnO_4$ 0.03405 gr. VO_2 = 21.06%
0.1274 gr. " " 0.02708 gr. " = 21.26%

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0.0840 gr.	gave with	$KMnO_4$	0.01778 gr. VO_2	= 21.16%
0.1532 gr.	"	"	0.0659 gr. V_2O_5	= 43.01%
0.1612 gr.	"	"	0.0689 gr. "	= 42.77%
0.1625 gr.	"	"	0.0699 gr. "	= 42.99%

In the determination of the water by fusion with sodic tungstate, the vanadic dioxide is oxidized to pentoxide. Hence it is necessary to add to the percentage of water found — 15.06 — the percentage of oxygen required to convert 21.16% (mean) of VO_2 to the equivalent quantity of V_2O_5 or 2.03%. This correction was not applied in the case of the first salt described above, because after a rapid fusion the vanadic dioxide appeared not to have been oxidized. In determining the vanadic pentoxide in these salts the oxide is first reduced to VO_2 by boiling with sulphurous acid and then titrated with hypermanganate. From want of material the phosphoric oxide in the green salt was determined by difference only.

The analyses of the green salt correspond with the formula

$$12\ P_2O_5\ .\ 14\ VO_2\ .\ 6\ V_2O_5\ .\ 7\ K_2O + 52\ aq,$$

which requires:

		Calc'd.	Mean.			
12 P_2O_5	1704	30.63	29.65 (diff.)			
14 VO_2	1166	20.96	21.16	21.06	21.26	21.16
6 V_2O_5	1096	19.71	19.73	19.82	19.80	19.58
7 K_2O	661	11.88	12.37	12.37		
52 H_2O	936	16.82	17.09	17.09		
	5563	100.00				

In this class of compounds I found it impossible to determine the sum of the acid-forming oxides by precipitating directly with mercurous nitrate and mercuric oxide. The results of many trials varied within very wide limits. Both the black and green salts are oxidized when heated with nitric acid and evaporated to degrees. Yellow crystalline masses remain, which contain phospho-vanadates, and which deserve a careful study as furnishing a new and perhaps better mode of forming that class of salts.

14 : 16 : 6 *Ammonic Phospho-vanadico-vanadate.* — When ammonic metavanadate or divanadate is boiled with a solution of ammonic orthophosphate in large excess, a colorless liquid is formed, which gives, with a solution of vanadic dioxide in chlorhydric acid, after a time, beautiful black or rather intensely deep green crystals, exactly resembling those of the potassic salt already described. The crystals

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dissolve easily in hot water free from saline matter, but do not crystallize readily from the solution. Of this salt, after careful washing and drying only,

0.7744 gr. lost with WO_4Na_2 0.1859 gr. = 24.01% $NH_3 + H_2O$. The oxygen gained by the vanadic dioxide is 2.14% and 24.01 + 2.14 = 26.15% $NH_3 + H_2O$

0.5556 gr. gave when heated in a combustion tube 0.1451 gr. = 26.11% $NH_3 + H_2O$

0.8969 gr. gave with $KMnO_4$ 0.2001 gr. VO_2 = 22.31%

0.2018 gr. " " 0.0444 gr. " = 22.19%

0.5626 gr. after reduction with SO_3H_2 gave with $KMnO_4$ 0.2427 gr. = 43.13% V_2O_5

0.2494 gr. after reduction with SO_3H_2 gave with $KMnO_4$ 0.1067 gr. = 42.76% V_2O_5

0.5325 gr. gave 0.0326 gr. $(NH_4)_2O$ = 6.13%

0.5053 gr. " 0.0309 gr. " = 6.12%

The mean of the two determinations of VO_2 is 22.25%, and the equivalent in V_2O_5 24.38%, which, subtracted from 42.76 and 43.13 respectively gives 18.38 and 18.75 for the percentages of V_2O_5.

The analyses correspond closely with the formula

$$14\ P_2O_5 \cdot 16\ VO_2 \cdot 6\ V_2O_5 \cdot 7(NH_4)_2O + 67\ aq,$$

which requires:

		Calc'd.	Found.	
14 P_2O_5	1988	33.21	33.06 (diff.)	
16 VO_2	1333	22.26	22.31	22.19
6 V_2O_5	1096	18.30	18.38	18.75
7 $(NH_4)_2O$	364	6.08	6.12	6.13
67 H_2O	1206	20.15	20.01	
	5987	100.00		

A portion of the very dark green salt was boiled with water, and the deep green solution allowed to stand, when much lighter green crystals separated. These were again dissolved and recrystallized. The crystals had a peculiar rusty olive-green surface color. Of this salt,

0.4770 gr. gave 0.1013 gr. V_2O_5 by $KMnO_4$ = 21.21% and

0.1014 gr. VO_2 = 21.22%

0.4014 gr. gave 0.0249 gr. $(NH_4)_2O$ = 6.20%

0.3062 gr. lost with WO_4Na_2 0.0663 gr. = 21.65%

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The determination of the sum of the water and ammonia must in this case be corrected for the oxygen required to convert the 21.22% of vanadic dioxide into vanadic pentoxide, since the ignition was continued with free access of air until the weight of the mass became constant. The correction is of course to be added, so that we have for the total loss $21.65 + 2.03 = 23.68\%$.

The analyses correspond tolerably well only with the formula

$$10\ P_2O_5\ .\ 11\ VO_2\ .\ 5\ V_2O_5\ .\ 5\ (NH_4)_2O + 41\ aq,$$

which requires:

		Calc'd.		Found.	
10 P_2O_5	1420	33.44		33.89	(diff.)
11 VO_2	916	21.57	76.50	21.21	76.32
5 V_2O_5	913	21.49		21.22	
5 $(NH_4)_2O$	260	6.12	23.50	6.20	23.68
41 H_2O	738	17.38		17.48	
	4247	100.00			

As the number of molecules of vanadic dioxide in this salt is uneven, it will be necessary to double the formula in order to obtain a symmetrical structural scheme.

ARSENIO-VANADICO-VANADATES.

The salts of this series are formed with great ease by mixing solutions of alkaline arsenates and vanadates, and adding a solution of vanadic dioxide in excess of chlorhydric acid. On evaporation large very dark green crystals are deposited in abundance. In preparing arsenio-vanadates it is difficult to avoid a partial reduction of the vanadic pentoxide by dust or other organic matter, and as a rule solutions are obtained which contain both classes of salts. The arsenio-vanadico-vanadates form a very beautiful and well-defined class of salts.

Analytical Methods. — Vanadic dioxide may be determined directly by titrition with hypermanganate after addition of sulphuric acid and appropriate dilution. To determine the arsenic present as arsenic pentoxide, the arsenic is first to be brought into the form of arsenous oxide by means of sulphurous acid after adding a little sulphuric acid to the solution. The arsenic may then be precipitated as sulphide by means of sulphydric acid, and weighed on a Gooch filter. The filtrate contains all the vanadium in the form of dioxide, which may then be determined by means of hypermanganate. The relation between the two oxides of vanadium is then easily found. The accurate determination

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of the water of crystallization in these salts is difficult. They all lose arsenic oxide when heated with sodic tungstate, and the only method which can be safely employed consists in heating weighed portions over a radiating cup of sheet-iron until a constant weight is obtained.

12 : 12 : 6 *Ammonium Salt.* — When ammonic metavanadate or divanadate is boiled with a large excess of ammonic arsenate, a colorless solution is formed. On adding a solution of vanadic dioxide in chlorhydric acid, a dark blue precipitate is formed, which dissolves readily in an excess of dilute chlorhydric acid. No precipitate is formed if the solution of the dioxide contains enough free acid. After standing some hours, a very dark green, almost black, crystalline salt is deposited in quantity. This is to be washed with cold water. The crystals exactly resemble those of the black potassic phospho-vanadico-vanadate already described. They are insoluble in saline solutions, and but slightly soluble in cold water. The solution has a greenish-yellow color. It gives a brick-red indistinctly crystalline precipitate with argentic nitrate, and a dull yellow flocky precipitate with mercurous nitrate. This last becomes crystalline on standing. It will serve to prepare other salts of this series by double decomposition with chlorides. The solution of the salt gives no precipitate with cupric sulphate or baric chloride. In this salt,

1.1623 gr.	gave with $KMnO_4$	0.2199 gr. VO_2	= 18.91%
0.8719 gr.	"	" 0.3605 gr. V_2O_5	= 41.37%
0.9726 gr.	gave	0.5500 gr. As_2S_3	= 52.87%
0.8246 gr.	"	0.4646 gr. "	= 52.68%
1.0209 gr.	"	0.0538 gr. $(NH_4)_2O$	= 5.27%

The vanadic pentoxide, after deducting the equivalent of the dioxide found, is 20.65%. The water could not be determined either by heating with sodic tungstate or in a combustion tube, as arsenous oxide sublimed in each case. It is therefore estimated by difference.

The analyses agree fairly well with the formula

$$12\ As_2O_5 \,.\, 12\ VO_2 \,.\, 6\ V_2O_5 \,.\, 5\ (NH_4)_2O + 7\ aq,$$

which requires:

		Calc'd.	Found.
12 As_2O_5	2760	52.65	52.68 52.87
12 VO_2	1000	19.08	18.91
6 V_2O_5	1096	20.91	20.65
5 $(NH_4)_2O$	260	4.96	5.27
7 H_2O	126	2.40	2.40
	5242	100.00	

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It will be observed that this salt may be considered as derived from twelve molecules of an arsenio-vanadate by reduction of one half the vanadic pentoxide to dioxide and loss of seven molecules of ammonic oxide, since we have

$$12\ \{As_2O_5 \cdot V_2O_5 \cdot (NH_4)_2O\} =$$
$$12\ As_2O_5 \cdot 12\ VO_2 \cdot 6\ V_2O_5 \cdot 5\ (NH_4)_2O + 7\ (NH_4)_2O + 6\ O.$$

This relation might be made available in the preparation of the salt. Boiling water instantly decomposes this compound, and gives a deep green solution, which on standing deposits crystals of a peculiar deep olive-green color with a tinge of brown. The black salt corresponds exactly in composition to a phosphorus compound above described, except only as regards water of crystallization:

$$12\ P_2O_5 \cdot 12\ VO_2 \cdot 6\ V_2O_5 \cdot 5\ (NH_4)_2O + 7\ aq.$$

9 : 9 : 8 *Ammonium-salt.* — When boiling water is poured upon the black salt, it instantly becomes deep olive-green upon the surface, and then dissolves to a deep green liquid, which on cooling deposits crystals with a dull olive-green surface color. These may be redissolved and recrystallized a second time. The mother liquor from these crystals has a bright green color, and contains much vanadic acid. In the olive-green salt,

0.4061 gr. gave 0.0167 gr. $(NH_4)_2O$ = 4.12%
0.2871 gr. " 0.1370 gr. As_2S_3 = 44.61%
0.2871 gr. " 0.1393 gr. V_2O_5 by $KMnO_4$ = 48.51% (complete oxidation)
0.1637 gr. gave 0.0259 gr. VO_2 by $KMnO_4$ = 15.82%

The analyses correspond tolerably well with the formula

$$9\ As_2O_5 \cdot 9\ VO_2 \cdot 8\ V_2O_5 \cdot 4\ (NH_4)_2O + 11\ aq,$$

which requires:

		Calc'd.		Found.	
9 As_2O_5	2070	44.17	60.17	44.61	60.43
9 VO_2	750	16.00		15.82	
8 V_2O_5	1461	31.17		31.17	
4 $(NH_4)_2O$	208	4.44		4.12	
11 H_2O	198	4.22		4.28 (diff.)	
	4687	100.00			

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The formula given must be doubled to give a structural scheme in which all the terms will be symmetrically arranged.

It appears at least probable that classes of antimonio-vanadates and antimonio-vanadico-vanadates also exist, but the few experiments which I have been able to make with the small quantity of material at my disposal are not conclusive as to either point, and I hope to be able to return to the subject.

VANADICO-VANADATES.

Salts belonging to this series are formed when solutions of vanadates are mixed with those of vanadic dioxide, and when vanadates undergo partial reduction by the action of any reducing agent. These compounds are often crystalline and well defined. They have, usually at least, a green color.

2 : 4 *Ammonic Vanadico-vanadate.* — When a solution of vanadic dioxide in chlorhydric acid is added to one of ammonic metavanadate, a fine green crystalline salt separates, but slightly soluble in either cold or hot water. The salt analyzed was not recrystallized, but merely washed with cold water and dried upon woollen paper. Of this salt,

1.0470 gr. gave 0.0159 gr. VO_2 by $KMnO_4$ = 15.21% VO_2
1.0470 gr. " 0.0701 gr. V_2O_5 " = 66.98% V_2O_5
0.1470 gr. " 0.0066 gr. $(NH_4)_2O$ = 4.50%

The analyses lead to the formula

$$4\ V_2O_5 \cdot 2\ VO_2 \cdot (NH_4)_2O + 8\ aq,$$

which requires

		Calc'd.	Found.
4 V_2O_5	730.4	66.82	66.98
2 VO_2	166.6	15.24	15.21
$(NH_4)_2O$	52	4.76	4.50
8 H_2O	144	13.18	13.31 (diff.)
	1093	100.00	

The following may serve as starting-points for further investigation. When solutions of sodic divanadate and manganous sulphate are mixed and allowed to stand in an open vessel, very dark green well-defined crystals are gradually deposited. There is here, doubtless, reduction from the presence of dust. When a solution of vanadic dioxide in chlorhydric acid is mixed with solutions of the sulphates of zinc, copper,

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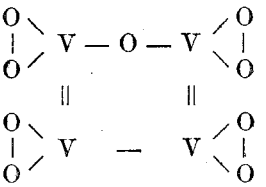
cobalt, or nickel, and of sodic divanadate, dark green crystalline precipitates are formed on standing, which would appear to be vanadico-vanadates, but which, as they are formed in the presence of an excess of a strong acid, may prove to be types of vanadico-vanadic acids. In his valuable paper on the salts formed by vanadic acid, Rammelsberg has described a remarkable compound, which may be regarded as an anhydride of a special form of vanadico-vanadic acid. This compound has the formula

$$V_2O_5 + 2\ VO_2,$$

and forms black microscopic crystals. Its structural formula may be written:



It is easy to see how acids of various types might be derived from such anhydrides by replacing oxygen by an equivalent of hydroxyl. The existence of very well defined series of phosphoroso-tungstates and phosphoroso-molybdates, and of similar series of compounds containing As_2O_3 and Sb_2O_3, would naturally lead to the attempt to form similar classes of complex acids containing V_2O_3. Want of material has prevented me from experimenting in this direction, and I must content myself with directing the attention of other chemists to the subject. Vanadic protoxide appears to possess the properties of a base only, but our knowledge of the subject is so imperfect that it may also be well worth while to determine whether there may not be a class of vanadium compounds corresponding to the hypophospho-tungstates and hypophospho-molybdates.

The existence of classes of phospho-vanadates and arsenio-vanadates embraced under the general formula

$$R_2O_5 \cdot V_2O_5 \cdot n\ H_2O$$

would seem to imply that of corresponding chlorides, bromides, etc., of corresponding or analogous types,

$$R'Cl_5 \cdot RCl_5,\quad R'Cl_4 \cdot RCl_5, \text{ etc.}$$

Various compounds of this kind have already been observed by chemists, though, so far as I am aware, no attempt has been made to classify

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them or to assign to them their true position as double chlorides, etc., corresponding to double oxides capable of forming complex acids. Examples of this class are the following: —

$SnCl_4$	+	PCl_5	Casselmann.
$SnCl_4$	+	$POCl_3$	"
$TiCl_4$	+	$POCl_3$	Weber.
$TiCl_4$	+	PCl_5	Tüttschew.
$SeCl_4$	+	$SbCl_5$	Weber.
$VOCl_2$	+	$PtCl_4$	Brauner.
Al_2Cl_6	+	2 $POCl_3$	Casselmann.
Fe_2Cl_6	+	2 $POCl_3$	"
$SbCl_5$	+	PCl_5	Weber.
$SbCl_5$	+	$POCl_3$	"

It is at least possible that in these and many similar cases complex or double acids correspond to the double chlorides, and it is probable that the action of such double chlorides upon solutions of acid tungstates and molybdates would produce complex acids containing tungsten or molybdenum and the two acid-forming oxides corresponding to the two united chlorides. I shall at another time specially consider the compounds of platinous and phosphorous chlorides discovered by Schützenberger.

In my paper upon the vanadium compounds of tungsten and molybdenum I have endeavored to show that many formulas may be reduced to the same types as those of the phospho-tungstates and phospho-molybdates, provided that we assume that a part at least of the vanadic pentoxide is to be regarded as replacing tungstic or molybdic oxide, or that we have the chemical equivalence expressed by the equation

$$m\ V_2O_2 . O_3 = m\ WO_3 = m\ MoO_3.$$

This hypothesis had the advantage of simplifying many formulas materially, but was wholly unsupported by any positive evidence. I have now shown that there exist classes of phospho-vanadates and arsenio-vanadates which do not contain tungstic or molybdic oxide, but which are exactly parallel to phospho-tungstates, vanadio-tungstates, etc. in composition. Thus we have the salt,

$$12\ V_2O_5 . P_2O_5 . 3\ BaO + 45\ aq;$$

and the acid,

$$20\ V_2O_5 . P_2O_5 . 6\ H_2O + 53\ aq;$$

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corresponding to

$$12\ WO_3 . P_2O_5 . 3\ BaO, \quad \text{and} \quad 20\ WO_3 . P_2O_5 . 6\ H_2O.$$

As regards the mode of replacement, however, our views must depend upon the special form of structural formulas which we provisionally adopt. With the view which I have taken of the subject, we may write for a phospho-vanadic acid assumed to have the formula

$$6\ V_2O_5 . P_2O_5 . 3\ H_2O,$$

corresponding to the phospho-tungstic acid

$$6\ WO_3 . P_2O_5 . 3\ H_2O,$$

the structural formula,

$$\begin{array}{l} \overline{} \\ VlO_2 - O - O - VlO_2 \\ \quad | \qquad\qquad\qquad | \\ VlO_2 - O - O - VlO_2 \\ VlO_2 - O - O - VlO_2 \\ \quad | \qquad\qquad\qquad | \\ 3\ (OH) \equiv PO \text{———————} OP \equiv (OH)\ 3, \end{array}$$

exactly like

$$\begin{array}{l} \overline{} \\ WO_2 - O - O - WO_2 \\ WO_2 - O - O - WO_2 \\ \quad | \qquad\qquad\qquad | \\ 3\ (OH \equiv PO \text{———————} OP \equiv (HO)\ 3. \end{array}$$

In the formula of the phospho-vanadic acid assumed, I have represented the complex V_2O_2 by Vl; and it is easy to see how, structurally, this may be regarded as hexatomic, and as replacing W^{VI} or Mo^{VI}, since we may reasonably suppose that we have

$$\begin{array}{l} O - V \equiv \\ \quad | \quad | \\ O - V \equiv . \end{array}$$

With this view of the subject $(V_2O_2)O_2 = WO_2 = MoO_2$, etc. This mode of formulating compounds containing vanadic pentoxide enables us, as I have shown, to reduce many complex salts to relatively simpler types, and is supported, as we shall presently see, by the formulas of a special class of vanadates exactly corresponding to meta-

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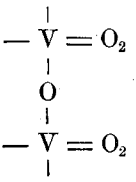
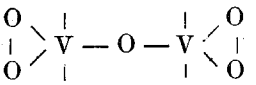
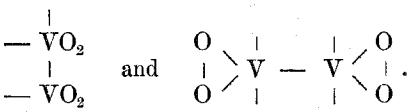
tungstates and metamolybdates. On the other hand, in by far the greater number of compounds thus far studied, the complex is to be regarded, I think, as built up of terms of the form RO_2, which may or may not be linked together by one or more atoms of oxygen. In certain cases, therefore, vanadic pentoxide may enter the complex with the structural formula



or as



This last view is strongly supported by the frequent presence of vanadic dioxide, two molecules of which may be considered as associated without a link of oxygen, as in the structural formulas



Finally, as I shall also prove, the structural formula must show what particular modification of phosphoric or vanadic oxide or acid is contained in the salt, since we have not merely ortho-phospho-tungstates but pyro-phospho-tungstates, various modifications of meta-phospho-tungstates, and corresponding compounds of molybdenum. It is at least probable that the different modifications of vanadic pentoxide or acid enter in a similar manner. These appear to be very numerous, and a wide field is thus opened for research. I shall return to this subject in the purely theoretical portion of my work.

If the view which I have taken as to the composition of the complex acids containing vanadium be correct, we ought to find some additional support for it in the constitution of the salts of vanadic acid. These have been studied by Roscoe, and especially by Norblad * and by Rammelsberg,† but the results obtained by these chem-

* Bidrag till kännedomen om Vanadiums Amfidsalter. Upsala Universitäts Årsskrift, 1873.

† Sitzungsberichte der Königl. Preuss. Akademie der Wissenschaften, 1883, p. 1.

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ists have not been systematized. The very numerous vanadates may be arranged, as I find, under seven groups or series. These are here given for the sake of comparison, typical salts actually obtained in each series being marked by the initials of the analysts. The existence of salts corresponding to other general formulæ is a matter of inference only. As will be seen at once, the first series corresponds to the group of metatungstates, if we compare $V_2O_2 . O_3$ with WO_3. Terms 1 and 3 of this series of vanadates have twice the usually given molecular weights.

First Series.

	Vanadates.	Metatungstates.
	R_2O . 4 V_2O_5	R_2O . 4 WO_3
R.	2 K_2O . 6 V_2O_5	2 R_2O . 6 WO_3
N.	3 Na_2O . 8 V_2O_5 + 24 aq	3 R_2O . 8 WO_3
R.	4 Na_2O . 10 V_2O_5 + 14 aq	4 R_2O . 10 WO_3
	5 R_2O . 12 V_2O_5	5 R_2O . 12 WO_3

Second Series.

N.	Na_2O . V_2O_5
R.	2 K_2O . 3 V_2O_5
R.	3 Li_2O . 5 V_2O_5
	4 R_2O . 7 V_2O_5

Third Series.

R.	K_2O . 2 V_2O_5 + 4 aq
R.	3 Li_2O . 4 V_2O_5 + 12 aq
R.	5 Li_2O . 6 V_2O_5 + 30 aq
	7 R_2O . 8 V_2O_5

Fourth Series.

R.	3 Li_2O . 2 V_2O_5 + 15 aq
	4 R_2O . 4 V_2O_5
	5 R_2O . 6 V_2O_5
	6 R_2O . 8 V_2O_5

Fifth Series.

R.	2 K_2O . V_2O_5 + 3 aq
	3 R_2O . 3 V_2O_5
	4 R_2O . 5 V_2O_5
	5 R_2O . 7 V_2O_5

Sixth Series.

	4 R_2O . 2 V_2O_5
R.	5 K_2O . 4 V_2O_5 + 7 aq
	6 R_2O . 6 V_2O_5
	7 R_2O . 8 V_2O_5

Seventh Series.

Ro.	3 Na_2O . V_2O_5 + 16 aq
	4 R_2O . 3 V_2O_5
	5 R_2O . 5 V_2O_5
	6 R_2O . 7 V_2O_5

The seven series which I have given embrace, I believe, all known types of vanadates. Each series may be represented by a general formula expressing the relation between the number of molecules of acid and basic oxides. These general formulæ are:

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I. $n\,R_2O\,.\,2\,n + 1\,.\,V_2O_5$
III. $n\,R_2O\,.\quad n + 1\,.\,V_2O_5$
II. $n\,R_2O\,.\,2\,n - 1\,.\,V_2O_5$
? $n\,R_2O\,.\,2\,n - 2\,.\,V_2O_5$
V. $n\,R_2O\,.\,2\,n - 3\,.\,V_2O_5$
IV. $n\,R_2O\,.\,2\,n - 4\,.\,V_2O_5$
VII. $n\,R_2O\,.\,2\,n - 5\,.\,V_2O_5$
VI. $n\,R_2O\,.\,2\,n - 6\,.\,V_2O_5$

The arrangement here given makes it probable that at least one series remains to be discovered. Fleitmann and Henneberg have described a phosphate having the formula $6\,Na_2O\,.\,5\,P_2O_5$. Such a compound would belong to a class of phosphates represented by the general formula — wanting among the vanadates —

$$n\,R_2O\,.\,2\,n - 2\,.\,P_2O_5.$$

Roscoe long since established the correspondence of the vanadates and phosphates up to a certain limit. Further investigation is required to show how complete the correspondence is. From an examination of the terms in the seven series of vanadates given above, it will appear that various isomeric modifications are probable among vanadates, and that these correspond, in *form* at least, to the various meta-phosphates, — mono, di, tri, tetra, and hexa-metaphosphates of Fleitmann and Henneberg. These chemists have also described a class of phosphates corresponding to the first term of the fourth series of vanadates given above. The sodium salt has the formula

$$3\,Na_2O\,.\,2\,P_2O_5 + 18\,aq.$$

In the imperfect state of our knowledge, all such coincidences are worthy of attention. Another conclusion may perhaps be safely drawn from the systematic arrangement of the vanadates which I have given. This is that meta, pyro, and ortho-vanadates, and the similar compounds of phosphorus, arsenic, antimony, etc., are not *isolated*, but are terms of more complete series. Thus the fifth series embraces the pyro-vanadates and their homologues, while the ortho-vanadates form the first term of the seventh series. In all the series given except the third, the common difference or homologizing term is $R_2O\,.\,2\,V_2O_5$; in the third series, it is $2\,R_2O\,.\,2\,V_2O_5$. In some cases only particular terms may exist to represent an entire series, because the special conditions necessary for the stability of other terms may be absent as regards degree. Taking now into account

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the analogy which I have shown to exist between $V_2O_2 . O_3$ and WO_3 or MoO_3, we may perhaps extend the above conclusions to the cases of the tungstates, molybdates, chromates, etc. Thus we may regard $K_2O . 2\ CrO_3$ as the initial term of a series corresponding to the third series of vanadates. If we double the usual formula of potassic terchromate, and write it $2\ K_2O . 6\ CrO_3$, we shall have the second term in a series corresponding to that of the metatungstates, the first term being the tetrachromate $K_2O . 4\ CrO_3$.

As a further support to my view that the metatungstates form a homologous series, I shall here describe two new tungstates obtained since the first part of this work was published.

16 : 3 : 4 *Sodio-ammonic Tungstate.* — I obtained this salt accidentally in attempting to prepare a series of glycero-phospho-tungstates. The thick syrupy liquid obtained by heating pulverized glacial phosphoric acid with glycerine, and allowing the mixture to stand for some days, was neutralized with ammonia and poured into a hot solution of 12 : 5 sodic tungstate. A beautiful white salt, in shimmering talcose scales, separated as the solution cooled. After careful draining, the salt was recrystallized for analysis. The crystals had a fatty lustre, and were quite easily soluble in hot water. No phosphoric acid could be found in the salt by the most careful testing, and no organic matter. In this salt,

2.3796 gr. lost on ignition	0.2825 gr.	= 11.87 %
2.1691 gr. " "	0.2568 gr.	= 11.84 %
2.1691 gr. gave	1.8209 gr. WO_3	= 83.94 %
2.0956 gr. "	0.0973 gr. $(NH_4)_2O$	= 4.64 %

The analyses correspond to the formula

$$16\ WO_3 . 3\ Na_2O . 4\ (NH_4)_2O + 18\ aq,$$

which requires:

		Calc'd.	Found.
16 WO_3	3712	83.79	83.94
3 Na_2O	186	4.20	4.21 (diff.)
4 $(NH_4)_2O$	208	4.69	4.64
18 H_2O	324	7.32	7.21
	4430	100.00	

This salt is especially interesting because it supplies a new term to the series of metatungstates, — the highest as yet obtained.

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12 : 1 : 4 *Sodio-ammonic Tungstate.* — This salt was obtained accidentally in an attempt to prepare a series of ethylo-phospho-tungstates. Syrupy phosphoric acid and absolute alcohol were mixed and heated for half an hour to about 80° C., and the mixture allowed to stand twenty-four hours. Ammonia was then added in small quantities at a time until in excess, the liquid being kept cool, the object being to form an ammonic ethylo-phosphate. The solution was then poured into one of 12 : 5 sodic tungstate. After a few minutes an abundant precipitation took place of small shimmering scales, which were drained on the filter-pump, washed with cold water, then dissolved in hot water and filtered. A very small quantity of a very insoluble salt in scales remained undissolved. The filtrate soon gave an abundance of small talcose scales with a fatty lustre.

Of this salt,

1.0293 gr. lost on ignition	0.1399 gr.	= 13.60 %
1.3019 gr. " "	0.1766 gr.	= 13.57 %
1.0001 gr. gave	0.0618 gr. $(NH_4)_2O$	= 6.18 %
1.0293 gr. "	0.8689 gr. WO_3	= 84.46 %

The analyses correspond to the formula

$$12\ WO_3 . Na_2O . 4\ (NH_4)_2O + 14\ aq,$$

which requires :

		Calc'd.	Found.
12 WO_3	2784	84.22	84.46
Na_2O	62	1.87	1.94 (diff.)
4 $(NH_4)_2O$	208	6.29	6.18
14 H_2O	252	7.62	7.42
	3306	100.00	

No trace of phosphoric acid could be detected in the salt, which is perhaps only interesting as furnishing additional evidence of the existence of a class of meta-tungstates in which the ratio of the tungstic oxide to the oxygen of the base is as 12 : 5. In this, as in the 16-atom salt above described, the presence of an excess of free ammonia explains the absence of phosphoric oxide in the compound formed.

My work on the compounds of vanadium is far less complete and thorough than I could have wished, on account of the relatively very high cost of the material. I indulge the hope that what I have done

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will be found at least substantially correct, and that the whole subject will soon receive the attention of other chemists, who may have a more abundant supply of vanadium salts at their disposal.

ARSENOSO-TUNGSTATES.

The alkaline salts belonging to this series are easily prepared by boiling arsenous oxide with strong solutions of acid tungstates, as, for example, with 12 : 5 or 10 : 4 sodic salt. The arsenous oxide should be in excess to secure complete saturation. The filtered solution on standing usually deposits crystals of arsenous oxide in greater or less quantity. The salts of this series are either colorless or pale yellow. They are not very easily oxidized in acid solutions, but in presence of an excess of alkali they absorb oxygen from the air and are converted into arsenio-tungstates. Bromine and chlorine readily oxidize such solutions. The arsenoso-tungstates are, as a rule, more soluble than arsenio-tungstates. They are very stable and well defined, and may as a class be embraced under the general formula

$$m\ WO_3 \cdot n\ As_2O_3 \cdot p\ R_2O,$$

in which n is usually greater than unity.

Analytical Methods. — Hydric sulphide precipitates arsenous sulphide from these salts, and usually without sensible reduction of the tungstic teroxide. It is best to precipitate from a hot solution, and to pass the current of the gas for a long time to insure complete decomposition. The arsenous sulphide may then be collected and weighed upon a Gooch asbestos filter. The tungstic oxide may be determined in the filtrate by mercurous nitrate in the usual manner. The simplest and most satisfactory method of determining the arsenic is by titrition with iodine in a solution containing an excess of sodic or potassic bicarbonate. Finally, it is possible to determine the arsenic by oxidizing the solution with bromine after adding an excess of an alkaline carbonate, and then precipitating the arsenic in the form of ammonio-magnesic arsenate. The precipitate must be redissolved in dilute chlorhydric acid and precipitated a second time.

The alkaline arsenoso-tungstates are, as a rule, easily soluble; the crystalline salts are often soft and gummy, though well defined. They appear in some cases to be decomposed more or less completely by solution and evaporation, with separation of arsenous oxide and formation of new salts of different series. In certain cases the addition of a salt of one of the heavy metals determines the precipitation of crystals

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of arsenous oxide in quantity. It is well known that alkaline hydrates also dissolve arsenous oxide in a proportion more than sufficient to form definite salts, and that the solutions deposit crystals of arsenous oxide on standing.

9 : 1 *Ammonic Arsenoso-tungstate.* — A boiling strong solution of 12 : 5 sodic tungstate dissolves arsenous oxide very readily, and in large quantity. The solution on evaporation gives a colorless or very pale yellow thick gummy mass, which on re-solution leaves octahedral crystals of arsenous oxide. The solution of the sodic salt gives with ammonic chloride, after standing some time, beautiful pale yellow almost colorless prisms. These may be redissolved and recrystallized without decomposition. Of this salt,

1.2699 gr. lost on ignition 0.2750 gr. = 21.65% H_2O, As_2O_3, and NH_3
1.3508 gr. gave by titrition with iodine 0.1034 gr. As_2O_3 = 7.65%
1.9457 gr. " 0.2713 gr. NH_4Cl = 6.78% $(NH_4)_2O$
0.9776 gr. " 0.7732 gr. WO_3 = 79.09% by $Hg_2(NO_3)_2$ and ignition.

The analyses lead to the formula

$$18\ WO_3 . 2\ As_2O_3 . 7\ (NH_4)_2O + 18\ aq,$$

which requires:

		Calc'd.	Found.
18 WO_3	4176	79.39	79.09
2 As_2O_3	396	7.53	7.65
7 $(NH_4)_2O$	364	6.92	6.78
18 H_2O	324	6.16	6.48
	5260	100.00	

The salt may of course be regarded as a double salt, but in this class of salts, as in the arsenio-tungstates and phospho-tungstates, I am disposed to think that in all cases we have an even number of molecules of tungstic oxide united with at least *two* molecules of arsenous oxide. Further investigations are of course required to settle this question. Meantime, from the analogy of the baric salt, we may write the formula provisionally as

$$9\ WO_3 . As_2O_3 . 4\ (NH_4)_2O + 9\ WO_3 . As_2O_3 . 3\ (NH_4)_2O + 18\ aq.$$

9 : 1 *Baric Arsenoso-tungstate.* — A solution of sodic arsenoso-tungstate obtained as above gives a white crystalline precipitate with baric chloride which is nearly insoluble in water, and which was there-

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fore only washed upon the filter and dried on woollen paper for analysis. In this salt,

1.1037 gr. ignited with WO_4Na_2 lost 0.1290 gr. = 11.69% H_2O
1.9764 gr. titrated with iodine gave 6.15%, 6.38%, 6.18% As_2O_3, mean 6.23%
1.5652 gr. gave 0.4358 gr. SO_4Ba = 18.28% BaO.

In determining the arsenous oxide the salt was first dissolved in very dilute chlorhydric acid, an excess of sodic bicarbonate being added before titrition. The analyses correspond with the formula

$$9\ WO_3 . As_2O_3 . 4\ BaO + 21\ aq,$$

which requires:

		Calc'd.	Found.
9 WO_3	2088	63.74	63.80
As_2O_3	198	6.04	6.23
4 BaO	612	18.68	18.28
21 H_2O	378	11.54	11.69
	3276	100.00	

The formula may be

$$18\ WO_3 . 2\ As_2O_3 . 8\ BaO + 42\ aq.$$

I have stated above that arsenoso-tungstates pass readily into arsenio-tungstates by oxidation and assumption of two additional atoms of oxygen. It seemed therefore natural to suppose that other simple or complex molecules might also be added to the molecule of arsenous oxide entering into the complex acid. I shall hereafter give the results of a detailed examination of this subject.

16 : 8 *Sodic Arsenoso-tungstates.* — Arsenous oxide dissolves readily in 10 : 4 sodic tungstate on boiling. When an excess of arsenic is present, the filtrate, after evaporation to the consistency of a syrup, deposits on spontaneous evaporation large colorless prismatic crystals. These dissolve readily in water without decomposition and may be recrystallized until perfectly pure. After four recrystallizations,

0.9451 gr. gave with CO_3NaH and iodine 0.2178 gr. As_2O_3 = 23.05%
0.6128 gr. " " " 0.1416 gr. " = 23.10%
1.1327 gr. gave 0.3237 gr. As_2S_3 = 23.01% As_2O_3
0.9225 gr. " 0.5005 gr. WO_3 = 54.26%
1.0614 gr. " 0.5781 gr. " = 54.46%
0.8517 gr. " 0.1238 gr. H_2O = 14.54%

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The analyses agree well with the formula

$$16\ WO_3 . 8\ As_2O_3 . 9\ Na_2O + 55\ aq,$$

which requires:

		Calc'd.	Found.		
16 WO_3	3712	54.23	54.28	54.46	
8 As_2O_3	1584	23.14	23.05	23.10	23.01
9 Na_2O	558	8.16		8.04 (diff.)	
55 H_2O	990	14.47		14.54	
	6844	100.00			

The salt gives off vapors of arsenous oxide even on gentle heating, and the determination of the water cannot be made by the use of sodic tungstate. After many trials, it was found best to mix the salt in a porcelain boat with plumbic oxide and carefully heat in a combustion tube, collecting the water in asbestos drenched with sulphuric acid. This process, suggested by my assistant, Mr. Herman Schmidt, gave good results in this case. A solution of the salt gives white flocky crystalline precipitates with baric, strontic, and calcic chlorides. Mercurous nitrate gives a pale yellow precipitate, which becomes darker on heating, and finally takes a dirty greenish-white color. Argentic nitrate gives a milk-white precipitate, which remains suspended for a long time. Manganous sulphate gives no precipitate, but the solution becomes yellow, and after standing some time yields beautiful bright yellow tabular crystals. Ammonic and potassic arsenates and orthophosphates give white crystalline precipitates, which appear to be respectively arsenoso-arsenio-tungstates and arsenoso-phospho-tungstates. The mother liquor of the 16 : 8 salt gives on evaporation a few crystals in a thick colorless syrup, which, after a few days, forms a pale yellowish hard gummy mass. This may prove to contain a second arsenoso-tungstate. The best method of preparing the beautiful 16 : 8 salt in quantity will probably be to mix 12 : 5 or 10 : 4 sodic tungstate and arsenous oxide in the precise ratio indicated by the formula of the salt, and, after adding water, to boil until the arsenous oxide is dissolved.

ARSENOSO-MOLYBDATES.

Arsenoso-molybdates are formed under the same conditions as arsenoso-tungstates, by boiling solutions of acid molybdates with an excess of arsenous oxide. In this case also there is always a sort of

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supersaturation, and arsenous oxide separates from the solution on cooling. The general statements made concerning the arsenoso-tungstates apply to these salts also. The general formula is

$$m\ MoO_3\ .\ n\ As_2O_3\ .\ p\ R_2O,$$

in which n is usually greater than unity. The salts are often beautifully crystalline.

Analytical Methods. — Arsenous oxide may be determined in these salts by oxidizing the solutions in presence of an excess of an alkaline carbonate by means of bromine, and precipitating as ammonio-magnesic arsenate. The precipitation must be repeated a second time, but the final treatment with ammonic sulphide, which I have recommended for the separation of phosphoric and molybdic oxides, is of course inadmissible. By far the best method of determining the arsenic in these salts is titrition with iodine after addition of an excess of an alkaline bicarbonate. It is not possible to determine the oxides of molybdenum and arsenic together by precipitation with mercurous nitrate, since no amount of care suffices to prevent the volatilization of arsenic in the subsequent ignition. For the same reason, it is also very difficult to determine the water of crystallization by the ignition loss, as fumes of arsenous oxide are given off at temperatures which are much below that at which sodic tungstate fuses. The degree of facility with which this takes place varies with the salt to be analyzed. As regards the determination of the water, I have found it best to heat gently in a porcelain crucible, supported over a small iron cup heated from below, but even in this case the results are never very satisfactory. Arsenous oxide cannot be separated from molybdic oxide by hydric sulphide, since molybdic sulphide is always precipitated at the same time, even when phosphoric acid has been added in excess. I have, however, found that fairly good determinations of molybdic oxide may be made in many cases by dissolving, boiling with a small excess of ammonia, adding a little ammonic chloride, and finally precipitating with baric chloride. The baric molybdate may then be ignited and weighed upon an asbestos filter. The results, if not very accurate, are at least sufficiently close to be of great service as verifications of formulas.

8 : 2 *Baric Arsenoso-molybdate.* — A boiling strong solution of 14 : 6 ammonic molybdate dissolves arsenous oxide in large quantity, and very readily. The solution has usually a yellowish-green color from slight reduction of the molybdic teroxide. After filtration and evaporation upon a water-bath, it deposits an abundance of octahedral crys-

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tals of arsenous oxide. The filtrate from these does not yield crystals on standing, but after evaporation upon the water-bath solidifies to a greenish gummy mass, readily soluble in water, often however leaving a residue of arsenous oxide. The solution of this gummy salt gives a white crystalline precipitate with baric chloride. The filtrate from this, after evaporation and standing, yields an abundance of beautiful very pale greenish crystals, which may be redissolved and recrystallized without decomposition. In this salt,

1.1230 gr. lost on heating 0.1126 gr. = 10.03%
1.0548 gr. gave 0.3258 gr. SO_4Ba = 20.28% BaO
0.3919 gr. " 0.0678 gr. As_2O_3 = 17.31%
0.5774 gr. " 0.0995 gr. " = 17.23%
0.9729 gr. " 1.0383 gr. MoO_4Ba = 51.74% MoO_3

The analyses lead to the formula

$$8\ MoO_3 \cdot 2\ As_2O_3 \cdot 3\ BaO + 13\ aq,$$

which requires:

		Calc'd.		Found.	
8 MoO_3	1152	51.41 } 69.08		51.74 } 69.01	
2 As_2O_3	396	17.67 }		17.31 17.23 }	
3 BaO	459	20.48		20.28	
13 H_2O	234	10.44		10.03	
	2241	100.00		99.32	

The arsenous oxide was determined in the first analysis by boiling with a solution of sodic dicarbonate, filtering, and titrating with iodine; in the second, by direct titrition without previous filtration. The baryta was separated by fusion with sodic carbonate, and weighed as sulphate. The water was found by heating over a radiator until a constant weight was obtained, as it was impossible to ignite with sodic tungstate without volatilization of arsenous oxide.

The salt requires a very large quantity of water for solution. The dry salt in fine powder boiled with argentic nitrate gives a beautiful yellow crystalline salt. Thallous nitrate yields, under the same circumstances, a very pale yellow, also crystalline salt. The mercurous salt is pale yellow, but not distinctly crystalline.

12 : 5 *Arsenoso-molybdate of Ammonium.* — When a solution of zincous sulphate is added to one of the gummy arsenoso-molybdate of ammonium, no precipitate is found at first, but after a time colorless

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crystals are formed which do not contain zinc, and which may be recrystallized without apparent decomposition. The salt dissolves in a large quantity of water to a colorless solution. It is only partially decomposed by boiling with mercurous nitrate. In this compound,

0.7105 gr. gave 0.0326 gr. $(NH_4)_2O$ = 4.58%
0.9785 gr. " 0.0455 gr. " = 4.65%
1.2612 gr. " 1.3720 gr. MoO_4Ba = 52.74% MoO_3
1.3081 gr. " 0.3856 gr. As_2O_3 = 29.48%
0.6044 gr. " 0.1787 gr. " = 29.55%

The analyses correspond fairly well with the formula

$$12\ MoO_3\ .\ 5\ As_2O_3\ .\ 3\ (NH_4)_2O + 24\ aq,$$

which requires:

		Calc'd.		Found.		
12 MoO_3	1728	52.28 } 82.21		52.74	} 82.24	
5 As_2O_3	996	29.94 }		29.48	29.55 }	
3 $(NH_4)_2O$	156	4.71		4.58	4.65	
24 H_2O	432	13.07		13.15		
	3306	100.00				

The reactions of this salt were studied by acting with metallic solutions upon the finely pulverized substance, so as to avoid, if possible, the decomposing action of water. In this manner cold solutions of argentic and thallous nitrates give beautiful colorless granular crystals. Baric chloride gives a white colorless salt more flocky than the ammonium compound. Manganous sulphate does not react in the cold, but on boiling for some time a beautiful pale canary-yellow crystalline salt is formed. Cupric sulphate does not act when cold, but on boiling a clear solution results.

6 : 3 *Arsenoso-molybdate of Manganese.* — A portion of the dry gummy mass of arsenoso-molybdate of ammonium, which had stood for some time in the laboratory, was redissolved and filtered from a small quantity of arsenous oxide. The filtrate gave no precipitate with manganous sulphate, but, on boiling, the fine green solution became much lighter in color, then turbid, and finally deposited very beautiful bright orange-colored octahedral crystals insoluble in water. Of this salt,

0.5961 gr. gave 0.2052 gr. As_2O_3 = 34.41%
0.7341 gr. " 0.1216 gr. $P_2O_7Mn_2$ = 8.28% MnO
0.6362 gr. lost on heating over a radiator 0.0428 gr. = 6.73%

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The analyses correspond to the formula

$$6\ MoO_3\ .\ 3\ As_2O_3\ .\ 2\ MnO + 6\ aq,$$

which requires:

		Calc'd.	Found.
6 MoO_3	864	50.59	50.58
3 As_2O_3	594	34.78	34.41
2 MnO	142	8.31	8.28
6 H_2O	108	6.32	6.73
	1708	100.00	

The molybdic oxide was determined by difference only. By mixing a solution of the gummy arsenoso-molybdate of ammonium with solutions of zincous and cupric sulphates respectively, after standing, beautiful octahedral crystals were deposited, which in the case of the zinc salt were colorless, in that of copper, of a fine green. The corresponding nickel salt was also in beautiful green octahedral crystals. In the zinc salt,

0.2378 gr. gave 34.52% As_2O_3 by titrition with iodine.
0.3115 gr. " 34.47% " " "
0.2169 gr. " 34.56% " " "

The formula

$$6\ MoO_3\ .\ 3\ As_2O_3\ .\ 2\ ZnO + 6\ aq$$

requires 34.38%. In the copper salt,

0.2619 gr. gave 34.67% As_2O_3 by titrition with iodine.
0.2006 gr. " 34.89% " " "

The formula

$$6\ MoO_3\ .\ 3\ As_2O_3\ .\ 2\ CuO + 6\ aq$$

requires 34.41%.

In the cases of both the zinc and copper salts a trace of free arsenous oxide was probably mixed with the salt analyzed. The nickel salt doubtless corresponds to the other three. In the case of the manganese salt, fumes of arsenous oxide were given off at very low temperatures. The pale canary-yellow manganese salt obtained by precipitating the 12 : 5 ammonic salts with manganous sulphate corresponded to the formula

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$$6\ MoO_3 . 3\ As_2O_3 . 2\ MnO + 15\ aq.$$

0.1727 gr. gave 31.77, 31.62, and 31.73% As_2O_3 by titrition with iodine.
1.1393 gr. " 0.0898 gr. $Mn_3O_4 = 7.33\%$ MnO.

The formula given requires 31.77% As_2O_3 and 7.59% MnO. The salt gave off arsenous oxide very freely when heated with sodic tungstate.

PHOSPHOROSO-TUNGSTATES.

I have already described the class of phosphoroso-molybdates, and will now consider the parallel group of phosphoroso-tungstates. The alkaline salts of this series are readily formed by the action of phosphorous and chlorhydric acids upon metatungstates of the higher order. They are, as a rule, better defined than the corresponding phosphoroso-molybdates, and are in all probability very numerous. The compounds to be described will be sufficient to open the subject for further investigation. The analytical methods employed were the same as in the case of the corresponding molybdenum salts, except that after oxidation of phosphorous to phosphoric acid, tungsten and phosphorus were usually precipitated together by mercurous nitrate and mercuric oxide.

22 : 4 : 6 *Ammonic Phosphoroso-tungstate.* — When the solution of phosphorous and chlorhydric acids formed by the action of water upon phosphoric terchloride is poured upon crystalline 12 : 5 ammonic tungstate, the salt packs at once into a dense mass. This is to be well rubbed up in a mortar with a large excess of the acid liquid, and allowed to stand for twenty-four hours. The greater part of the mass then presents large granular colorless crystals. A much smaller proportion of a white fine-grained salt is formed at the same time, and is easily separated by washing from the heavier crystals of the granular salt. This last may be washed with cold water on the filter pump, and dried on woollen paper. In mass the crystals present a faint but distinct tinge of yellow. The salt is but slightly soluble in cold water, but dissolves in a rather large proportion of boiling water to a yellow liquid. The solution gives no precipitate with cupric sulphate, but the mixed liquid becomes somewhat darker on boiling. With argentic nitrate it gives a turbid solution, which becomes purplish on heating, and finally gives a dark dull-purple precipitate. With mercurous nitrate the solution gives a white light precipitate, which becomes deep yellow on heating, and regains its white color on cooling. In this salt,

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1.6407 gr. gave 0.1136 gr. $P_2O_7Mg_2$ = 5.12% PO_3H_3
1.7666 gr. " 0.1256 gr. " = 5.26% "
1.5933 gr. " 0.0791 gr. $(NH_4)_2O$ = 4.96%
1.7340 gr. lost with WO_4Na_2 0.2253 gr. = 12.99%

The analysis is of course subject to the corrections indicated by the equation

$$2\ PO_3H_3 = P_2O_5 + OH_2 + 4\ H.$$

The results agree very well with the formula

$$22\ WO_3 . 4\ PO_3H_3 . 6\ Am_2O + 25\ aq,$$

or

$$22\ WO_3 . 4\ \{H . PO . 2\ OH\}\ 6\ (NH_4)_2O + 25\ aq,$$

which requires:

		Calc'd.	Found.
22 WO_3	5104	82.40	82.46
4 PO_3H_3	328	5.29	5.26 5.12
6 $(NH_4)_2O$	312	5.04	4.96
25 H_2O	450	7.27	7.32
	6194	100.00	

The phosphorous acid was oxidized by bromine after adding an excess of sodic carbonate. The salt is quietly decomposed by heating, giving a mixture of WO_3 . W_2O_5 and P_2O_5.

32 : 16 : 5 *Potassic Phosphoroso-tungstate.* — This salt was formed, like the ammonium salt, by the action of a mixture of phosphorous and chlorhydric acids upon crystallized 10 : 4 potassic tungstate. In this case, also, two salts appear to be formed, — a heavier colorless crystalline salt in relatively large quantity, and a lighter fine-grained salt easily removed by careful washing. Of these, only the first was examined. Of this salt,

1.4225 gr. gave 1.2124 gr. oxides = 85.23% $WO_3 + P_2O_5$
1.3877 gr. " 0.2428 gr. $P_2O_7Mg_2$ = 11.19% P_2O_5 = 12.96% PO_3H_3
1.3949 gr. lost 0.1406 gr. = 10.08%

The analyses correspond to the formula

$$32\ WO_3 . 16\ PO_3H_3 . 5\ R_2O + 46\ aq,$$

or

$$32\ WO_3 . 16\ \{H . PO . 2\ OH\}\ 5\ R_2O + 46\ aq,$$

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which requires:

		Calc'd.	Found.
32 WO_3	7424	73.97	74.04
16 PO_3H_3	1312	13.07	12.96
5 R_2O	472	4.70	4.69 (diff.)
46 H_2O	828	8.26	8.31
	10036	100.00	

The salt is but slightly soluble even in boiling water. It has no yellow tint.

22 : 8 : 2 *Sodic Phosphoroso-tungstate.* — This salt was formed, like the last, by the action of a mixture of phosphorous and chlorhydric acids upon crystallized 10 : 4 sodic tungstate. The action is very energetic. The colorless crystals of the tungstate soon disappear, and are replaced by yellow granular crystals in large quantity. The yellow crystals were well washed upon the filter-pump with cold water, and dried on woollen paper. Of this salt,

1.7082 gr. gave 1.4895 gr. oxides = 87.19 % $WO_3 + P_2O_5$
1.3623 gr. " 0.1870 gr. $P_2O_7Mg_2$ = 8.78 % P_2O_5 = 10.15 % PO_3H_3
1.3532 gr. lost with WO_4Na_2 0.1481 gr. = 10.94 %

The analyses correspond to the formula

$$22\ WO_3 . 8\ PO_3H_3 . 2\ Na_2O + 35\ aq,$$

which requires:

		Calc'd.	Found.
22 WO_3	5104	78.36	78.40
8 PO_3H_3	656	10.07	10.15
2 Na_2O	124	1.90	1.87 (diff.)
25 H_2O	630	9.67	9.58
	6514	100.00	

The sodium salt is nearly insoluble in cold water, and but slightly soluble in boiling water. The undissolved portion takes a much brighter yellow color. As in the cases of the potassium and ammonium salts, a small quantity of a second salt, in very small crystals and of a white color, is formed at the same time.

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PHOSPHOROSO-MOLYBDATES (*again*).

As the phosphoroso-molybdate of ammonium, which I have described in another part of this paper, appeared to contain a trace of phosphoric acid, I repeated the preparation with a perfectly pure solution of phosphorous acid obtained by the action of water upon phosphorous chloride. The liquid contained, of course, free chlorhydric acid, and was poured into a cold strong solution of 14 : 6 ammonic molybdate. A sulphur-yellow precipitate was at once formed, consisting of very minute talcose scales. The salt was washed on the filter-pump very thoroughly with cold water, and dried on woollen paper. It is readily soluble in hot water to a yellow liquid. The solution on boiling reduces mercuric chloride to mercurous chloride. It gives an abundant white, flocky precipitate with argentic nitrate, which on long boiling becomes darker. Finally, silver is reduced. In this preparation,

0.7247 gr. lost with WO_4Na_2 0.1150 gr. = 15.87 %
0.8323 gr. gave 0.0386 gr. $(NH_4)_2O$ = 4.64 %
0.7426 gr. " 0.0776 gr. $P_2O_7Mg_2$ = 6.68 % P_2O_5
0.9517 gr. " 0.0994 gr. " = 6.68 % "

The phosphorous acid was oxidized by bromine in presence of an excess of CO_3NaH. The analyses correspond most nearly to the formula

$$24\ MoO_3 . 4\ PO_3H_3 . 4\ (NH_4)_2\ O + 25\ aq,$$

which requires:

		Calc'd.		Found.	
24 MoO_3	3456	77.80	85.18	77.45	85.16
4 PO_3H_3	328	7.38		7.71	
4 $(NH_4)_2O$	208	4.68	14.82	4.64	14.84
25 H_2O	450	10.14		10.20	
	4442	100.00			

The analyses confirm the formula first obtained, though the new salt contains eight molecules more of water of crystallization.

ANTIMONOSO-TUNGSTATES.

When solutions of an acid tungstate of sodium are boiled with antimonious oxide, the latter very slowly dissolves, and it is difficult to obtain perfectly saturated solutions. It is best to employ antimonious

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oxide which has been freshly precipitated from the corresponding chloride by sodic carbonate and washed by decantation with cold water. If the precipitated oxide is allowed to stand for some time, it becomes crystalline, and is then no longer available. The solution of antimonoso-tungstate obtained in this manner has a yellow color, and there is no sensible reduction of tungstic teroxide. Instead of this process, the following may be employed with advantage. Freshly precipitated antimonious oxychloride, SbOCl, after washing with cold water, dissolves very readily in boiling solutions of alkaline tungstates of the metatungstic series. The solutions obtained in this way are also yellow. The oxychloride, on standing for some days, also becomes highly crystalline, and then dissolves with great difficulty. The solutions of sodic salts obtained as above become on evaporation thick and syrupy, and finally yield yellow gummy masses. There is in these cases also a tendency to supersaturation, as with the arsenoso-tungstates, though by no means to the same extent, and crystals of antimonious oxide (hydrate?) are sometimes deposited. The concentrated solution of the sodic salt obtained as above gives yellow oils with strong solutions of potassic or ammonic salts, which are but slightly soluble in a large excess of the latter. After pouring off the supernatant liquid, the oils may be redissolved in a small quantity of water, and again precipitated by a large excess of a concentrated solution of a potassic salt. I prefer for this purpose the bromide. Two or three repetitions of this process yield a nearly pure potassic antimonoso-tungstate, which may be advantageously used in the preparation of other salts. The alkaline salts of this series are either oily liquids or gummy masses with a pale yellow color, and very easily soluble. The solutions absorb oxygen rather slowly from the air, and are not easily oxidized by bromine or chlorine unless in presence of an excess of alkali, as, for example, sodic bicarbonate. They then pass into antimonio-tungstates. The general formula of the antimonoso-tungstates is

$$m\,WO_3 . n\,Sb_2O_3 . p\,R_2O.$$

Analytical Methods. — The quantitative separation of antimony from tungsten in these compounds may be effected by the following methods. Hydric sulphide passed through the solution previously acidulated with chlorhydric acid precipitates antimonious sulphide completely, without any sensible reduction or precipitation of tungsten. An aliquot portion of the sulphide may then be heated in an atmosphere of dry carbonic dioxide, in the usual manner. This method applies to the

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greater number of cases. In its place we may often, but not always, employ the following, which usually gives good results in the cases of the alkaline salts. Potassic cyanide, as free as possible from carbonate and cyanate, is to be fused in a crucible of Berlin porcelain, and then allowed to cool. A weighed portion of the antimonoso-tungstate is then to be placed upon the fused mass, and the whole cautiously heated to low redness, and kept for a short time at this temperature. The antimony is completely reduced to metal, and after the solution of the alkaline salts in cold water, and washing at first with water and afterward with alcohol, may be weighed upon an asbestos filter. It will be seen that this process is the same as that devised many years ago by myself for the separation of tin from tungsten, worked out in my laboratory by Mr. F. H. Talbutt,* and known as Talbutt's method. The process unfortunately does not apply to cases in which insoluble compounds are formed together with the reduced metallic antimony. As a rule, when the process is successful, the antimony is finally in the form of large bright metallic globules, but in some cases it forms on reduction wholly or partially a black powder containing tungsten, and the method then fails. In these cases an accurate result may be obtained by mixing the salt or the potassic cyanide with a quantity of potassic or sodic carbonate sufficient to completely saturate both the tungstic and antimonic oxides present. This variation in the application of the method is due to my assistant, Mr. Herman Schmidt. In determining antimonious or antimonic oxides by this process, there is, of course, the disadvantage that a higher is always estimated from a lower molecular weight. The following analyses will serve to show the degree of accuracy which may be obtained under favorable circumstances, the method applying to antimonio-tungstates as well as to the antimonoso series. In an antimonio-tungstate of potassium not of definite constitution,

1.0924 gr. gave 0.4407 gr. metallic antimony = 53.79 % Sb_2O_5
1.0316 gr. " 0.4155 gr. " " = 53.71 % "

In another compound,

0.9059 gr. gave 0.2251 gr. metallic antimony = 33.13 % Sb_2O_5
1.0312 gr. " 0.2558 gr. " " = 33.08 % "

Antimonious oxide may also be determined in these compounds by titrition with iodine, after adding to the solution an alkaline tartrate

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and an excess of sodic bicarbonate. It will be found advantageous to standardize the solution of iodine by means of pure crystallized antimonio-potassic tartrate, — of course, after addition of an alkaline dicarbonate.

The determination of tungstic oxide may be effected by first separating the antimony as sulphide, and then precipitating the hot solution with baric chloride, after adding ammonia in small excess. The baric tungstate may be weighed upon an asbestos filter. It is better, however, to precipitate the tungstic oxide by means of mercurous nitrate; only, in case this method is to be applied, the antimony must be precipitated as sulphide after the addition of dilute sulphuric acid, and chlorhydric acid must not be employed.

11 : 3 *Baric Antimonoso-tungstate.* — A solution of sodic antimonoso-tungstate, obtained as above, gives with baric chloride a heavy pale yellow curdy or indistinctly crystalline precipitate. This salt melts under hot water to a thick yellow oily liquid, which dissolves very slowly, requiring a large quantity of water for solution. The solution has a yellow color and an acid reaction. It gives pale yellow flocky precipitates, with mercurous, argentic, and thallous nitrates. Of this salt,

1.0722 gr.	lost on ignition with WO_4Na_2	0.0858 gr.	= 8.00 %
1.2057 gr.	gave	0.3318 gr. Sb_2S_3	= 21.78 % Sb_2O_3
1.3668 gr.	"	0.3371 gr. "	= 21.17 % "
1.2543 gr.	"	0.1440 gr. SO_4Ba	= 7.54 % Ba O
1.4895 gr.	"	0.1709 gr. "	= 7.53 % "
1.9450 gr.	"	1.6599 gr. oxides ($WO_3 + Sb_2O_4$)	= 85.34 %

The analyses lead to the formula

$$11\ WO_3 . 3\ Sb_2O_3 . 2\ BaO + 18\ aq,$$

which requires:

		Calc'd.		Found.		
11 WO_3	2552	63.07	84.42	62.79	62.99	(diff.)
3 Sb_2O_3	864	21.35		21.17	21.78	84.37
2 BaO	306	7.57		7.54	7.53	
18 H_2O	324	8.00		8.00		
	4046	100.00				

The salt may be reduced to the type

$$6\ WO_3 . Sb_2O_3 . BaO + 9\ aq,$$

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if we suppose Sb_2O_3 partially to replace WO_3; but in view of the very frequent recurrence of 22 molecules of tungstic oxide among complex inorganic acids, I am disposed to double the formula given above, and to write

$$22\ WO_3 . 6\ Sb_2O_3 . 4\ BaO + 36\ aq.$$

In the yellow oily salt obtained by precipitating sodic antimonoso-tungstate by means of potassic bromide, and carefully washing with a cold strong solution of the bromide, the ratio of the tungstic to the antimonious oxide was determined and found to be nearly 8 WO_3 to 2 Sb_2O_3, so that there is probably a series of antimonoso-tungstates with the general formula

$$8\ WO_3 . 2\ Sb_2O_3 . n\ R_2O.$$

The quantity of solution taken gave 0.1091 gr. Sb_2S_3 = 0.0935 gr. Sb_2O_3, and 0.3417 gr. WO_3 = 71.51 % WO_3 and 21.49 % Sb_2O_3.

ANTIMONOSO-MOLYBDATES.

The salts of this series are readily formed by boiling antimonious oxychloride, SbOCl, with an acid molybdate. The conditions are exactly the same as in the case of the corresponding antimonoso-tungstates. There is almost always a greater or less reduction of the molybdic oxide, and the solutions obtained have a greenish or greenish-blue tint from the presence of Mo_2O_5 or a similar oxide. The ordinary acid ammonic molybdate of commerce in cold solution readily dissolves freshly precipitated antimonious oxide with only a slight reduction of the molybdic oxide; on boiling, much reduction takes place.

Analytical Methods. — Antimonious oxide cannot be separated from molybdic oxide by means of hydric sulphide, as a greater or less proportion of molybdic sulphide is always found. By proceeding in the manner already pointed out for the separation of antimony from tungsten, it is possible, in many cases at least, to separate antimony from molybdenum with a very satisfactory degree of accuracy. It will be found, however, always advantageous to add a quantity of potassic or sodic carbonate sufficient to neutralize both the molybdic and antimonious oxides before fusion with potassic cyanide. Crucibles of the best Berlin porcelain are alone adapted to fusions of this kind, and even when these are employed the action of the alkaline mixture upon the crucible must be taken into account. The best method is to add

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to the solution an alkaline tartrate, and then to render it alkaline with an excess of sodic bicarbonate. The antimonious oxide may then be determined by titrition with iodine.

17 : 3 *Ammonic Antimonoso-molybdate.* — This salt crystallizes from a solution of antimonious oxide in 14 : 6 ammonic molybdate, in pale greenish-yellow granular crystals, but its preparation is rather uncertain. It is insoluble in cold water: for analysis, the crystals were simply washed and dried upon woollen paper. In this salt,

0.7474 gr. gave by titrition with iodine 0.1618 gr. Sb_2O_3 = 21.65 %
0.5287 gr. " 0.0399 gr. $(NH_4)_2O$ = 7.55 %
1.0869 gr. lost on ignition with MoO_4Na_2 and WO_4Na_2 0.1851 gr. = 17.03 %.

The analyses lead to the formula

$$17\ MoO_3 \cdot 3\ Sb_2O_3 \cdot 6\ (NH_4)_2O + 21\ aq,$$

which requires:

		Calc'd.	Found.
17 MoO_3	2448	61.18	61.32
3 Sb_2O_3	864	21.59	21.65
6 $(NH_4)_2O$	312	7.79	7.55
21 H_2O	378	9.44	9.48
	4002	100.00	

The molybdic oxide is estimated by difference. The solution from which this salt of ammonium separated gave, after twenty-four hours, a fine yellow crystalline precipitate with manganous sulphate. The formula given may be reduced to the type

$$18\ MoO_3 \cdot 2\ Sb_2O_3 \cdot 6\ (NH_4)_2O + 21\ aq,$$

if we assume that one molecule of Sb_2O_3 plays the part of, or replaces, one molecule of molybdic oxide. In determining the water in this salt I employed a mixture of equal molecules of sodic tungstate and molybdate, which fuses at a temperature below that at which molybdic oxide is given off.

In formulating the arsenoso-tungstates and arsenoso-molybdates I have assumed provisionally that normal arsenites are represented by one or another of the three general formulas

$$As_2O_3 \cdot R_2O, \qquad As_2O_3 \cdot 2\ R_2O, \qquad As_2O_3 \cdot 3\ R_2O,$$

the three plumbic arsenites forming appropriate special instances. This view would establish a broad line of distinction between arsenites

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and phosphites, which last are now generally considered as hydryl-phosphinates, the general formula being

$$H \cdot PO \cdot (OH)_2.$$

On the other hand, the existence of alkyl-arsinic acids appears to prove beyond a doubt that at least *some* arsenites belong to the same type with the phosphites. The older view must in any case be true for certain classes of salts, because the arsenites are not all reducible to the type $H \cdot AsO \cdot (OH)_2$, even if we admit that the atom of hydrogen is replaceable by an atom of univalent metal, for which there is no sufficient evidence in the case of the phosphites. If we consider the arsenic in the arsenoso-tungstates and arsenoso-molybdates which I have described to exist in the form of hydryl-arsinic acid, we shall have for the corresponding acids, respectively, the formulas

$$\begin{aligned}
18\ WO_3 \ .\ \ 4\ \{H \cdot AsO \cdot (OH)_2\} \cdot 8\ H_2O \\
16\ WO_3 \ .\ 16\ \{H \cdot AsO \cdot (OH)_2\} \cdot 9\ H_2O \\
\ 8\ MoO_3 \ .\ \ 4\ \{H \cdot AsO \cdot (OH)_2\} \cdot 3\ H_2O \\
12\ MoO_3 \ .\ 10\ \{H \cdot AsO \cdot (OH)_2\} \cdot 3\ H_2O \\
\ 6\ MoO_3 \ .\ \ 6\ \{H \cdot AsO \cdot (OH)_2\} \cdot 3\ H_2O
\end{aligned}$$

in which, of course, the basicity is purely arbitrary, since it depends in each case upon the number of molecules of base in a single salt. The internal basicity, as measured by the hydroxyl in the arsenical term, is always two, corresponding to one in the old style of writing. As the salts described appear to give off all their water when heated without other decomposition than loss from the volatilization of arsenous oxide, it would seem to follow that their formulas must then at least be written as if they contained all the arsenic as As_2O_3, since

$$2\ \{H \cdot AsO \cdot (OH)_2\} = As_2O_3 + 3\ H_2O.$$

PHOSPHOROSO-PHOSPHO-TUNGSTATES.

24 : 1 : 2 : 5 *Potassic Phosphoroso-phospho-tungstate.* — When a solution containing both phosphorous and orthophosphoric acids is added to one of 12 : 5 sodic tungstate, no precipitate is formed, but on adding potassic bromide a white crystalline salt is thrown down, slightly soluble in cold water, but soluble in a large quantity of boiling water, forming a turbid liquid which has an acid reaction. The solution gives no precipitate with cupric sulphate, even on boiling and with or without free chlorhydric acid. It gives a white flocky precipitate with

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argentic nitrate, which becomes darker on boiling, and finally deep chocolate-brown. This reaction resembles that of the phospho-hypo-phospho-tungstates. The solution gives a very pale yellow indistinctly crystalline precipitate with mercurous nitrate, which is not reduced by boiling, and a white flocky precipitate with baric chloride. The salt dissolves with much difficulty in ammonia-water, but easily in solutions of alkaline carbonates. Chlorhydric acid gives a white precipitate in these solutions, readily soluble in ammonia. In this salt,

1.5373 gr. lost on ignition 0.0578 gr. = 3.76%
1.5373 gr. gave 1.3702 gr. mixed oxides = 89.13% WO_3 and P_2O_5
1.7603 gr. " 0.1138 gr. $P_2O_7Mg_2$ = 4.13% P_2O_5
2.7325 gr. " 0.0836 gr. " = 1.96% "

In determining PO_3H_3 the solution in CO_3Na_2 was oxidized by bromine.

The analyses correspond with the formula

$$24\ WO_3 . 2\ PO_3H_3 . P_2O_5 . 5\ K_2O + 13\ aq,$$

which requires:

		Calc'd.		Found.	
24 WO_3	5568	84.75	86.91	85.00	86.96
P_2O_5	142	2.16		1.96	
2 PO_3H_3	164	2.49		2.50	
5 K_2O	472	7.18		7.11	
13 H_2O	224	3.41		3.43	
	6570	100.00			

When a solution of phosphorous and chlorhydric acids is mixed with one of the 24 : 1 phospho-tungstate of sodium,

$$24\ WO_3 . P_2O_5 . 2\ Na_2O + 27\ aq,$$

no precipitate is formed, but after a time relatively large colorless measurable crystals of the phospho-tungstate are deposited.

PHOSPHOROSO-PHOSPHO-MOLYBDATES.

72 : 3 : 2 : 9 *Ammonic Phosphoroso-phospho-molybdate.* — When the solution of phosphorous and chlorhydric acids obtained by treating phosphorous terchloride with cold water is mixed with a solution of 10 : 2 ammonic phospho-molybdate, a greenish-yellow crystalline pre-

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cipitate is thrown down at once. The salt is very insoluble in water. It was washed upon the filter-pump and dried on woollen paper for analysis. In this salt,

1.0222 gr. lost with WO_4Na_2 0.0975 gr. = 9.54%
0.8936 gr. gave 0.0354 gr. $(NH_4)_2O$ = 3.96%
1.1348 gr. " 0.0646 gr. $P_2O_7Mg_2$ = 3.63%
1.2439 gr. " 0.0696 gr. " = 3.58%

The determination of phosphoric oxide was made after oxidation by bromine.

The analyses agree very well with the formula

$$72\ MoO_3 . 2\ PO_3H_3 . 3\ P_2O_5 . 9\ (NH_4)_2O + 38\ aq,$$

which requires:

		Calc'd.	Found.
72 MoO_3	10368	85.61	85.56
3 P_2O_5	426	3.52	3.58 3.63
2 PO_3H_3	164	1.35	1.50
9 $(NH_4)_2O$	468	3.87	3.96
38 H_2O	684	5.65	5.58
	12110	100.00	

The formation of this salt may be represented by the equation

$$3\ \{24\ MoO_3 . P_2O_5 . 3\ (NH_4)_2O\} + 2\ PO_3H_3 =$$
$$72\ MoO_3 . 3\ P_2O_5 . 2\ PO_3H_3 . 9\ (NH_4)_2O.$$

PHOSPHO-HYPOPHOSPHO-TUNGSTATES.

26 : 4 : 2 *Potassic Phospho-hypophospho-tungstate.* — When the 24 : 1 phospho-tungstate of sodium is boiled with an excess of a solution of hypophosphorous acid and a solution of potassic bromide is added to the clear pale blue filtrate, a white crystalline precipitate is after a time thrown down. The salt dissolves readily in hot water to a clear solution. This gives a white flocky crystalline precipitate with baric chloride, a pale yellow precipitate with mercurous nitrate, and a white precipitate with argentic nitrate, which on boiling becomes first yellow, then brown, and finally takes a brownish color, and deposits a precipitate closely resembling ferric hydrate. Cuprous sulphate is without action on the solution. For analysis the freshly formed salt

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was thrown upon a filter, washed on the filter-pump thoroughly with cold water, and finally dried for analysis upon woollen paper. Of this preparation,

1.2162 gr.	gave 0.9706 gr.	mixed oxides	= 79.81%	
1.9865 gr.	" 1.5903 gr.	"	= 80.05%	
1.0921 gr.	" 0.1408 gr.	$P_2O_7Mg_2$	= 8.25%	P_2O_5
1.5059 gr.	" 0.1552 gr.	"	= 6.59%	"
1.2162 gr.	" 0.6340 gr.	$PtCl_6K_2$	= 10.12%	K_2O
0.9633 gr.	" 0.5074 gr.	"	= 10.22%	"
1.2705 gr.	lost with WO_4Na_2	0.1138 gr.	= 8.96%	
0.8472 gr.	" " "	0.0778 gr.	= 9.18%	

In the analyses the hypophosphorous acid was determined by oxidation with bromine, after adding an excess of sodic carbonate. The total phosphoric acid was then determined as ammonio-magnesic phosphate. In another portion of the salt the phosphoric acid proper was precipitated directly by magnesia-mixture in the usual manner. Corrections are of course made for the loss of hydrogen in ignition, according to the equation

$$2\ PO_2H_3 + H_2O = P_2O_5 + 8\ H,$$

and also for the retention of one atom of oxygen by the mixed oxides, as shown by the same equation.

The analyses correspond to the formula

$$26\ WO_3 \cdot 2\ PO_2H_3 \cdot 4\ P_2O_5 \cdot 9\ K_2O \cdot Na_2O + 43\ aq,$$

or,

$$26\ WO_3 \cdot 2\ \{H_2 \cdot PO \cdot OH\} \cdot 4\ P_2O_5 \cdot 9\ K_2O \cdot Na_2O + 43\ aq,$$

which requires:

		Calc'd.	Found.
26 WO_3	6032	71.66	71.56 71.80
4 P_2O_5	568	6.74	6.59
2 PO_2H_3	132	1.57	1.55
9 K_2O	850	10.09	10.12 10.22
Na_2O	62	0.74	0.78 (diff.)
43 H_2O	774	9.20	9.23
	8418	100.00	

It cannot be doubted that similar compounds containing molybdenum in place of tungsten remain to be discovered. I did not, how-

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ever, succeed in obtaining them by the action of hypophosphorous acid upon phospho-molybdates, and the precise conditions necessary are yet to be determined. It appears to be at least probable that classes of phosphoroso-hypophospho-tungstates and phosphoroso-hypophospho-molybdates will sooner or later be discovered.

ARSENOSO-PHOSPHO-TUNGSTATES.

The salts of this series are formed when solutions of orthophosphates and arsenoso-tungstates are mixed, and when arsenous oxide is boiled with a solution of an alkaline phospho-tungstate. The alkaline salts are sometimes crystalline and sometimes gummy. The series is probably a very extensive one.

Analytical Methods. — In these salts the arsenous oxide is best determined by titrition with iodine after adding an excess of an alkaline dicarbonate. After separating arsenous oxide as sulphide by sulphydric acid, the phosphoric oxide may be determined by magnesia-mixture. Phosphoric and tungstic oxides may be determined together by mercurous nitrate and mercuric oxide after separating arsenous oxide from the solution as arsenous sulphide, dilute sulphuric acid being employed in place of chlorhydric acid. Water is best determined by heating over a radiator.

32 : 14 : 3 : 10 *Potassic Arsenoso-phospho-tungstate.* — This salt was prepared by boiling potassic phospho-tungstate with an excess of finely pulverized arsenous oxide. The filtered solution had a pale greenish-yellow tint, and after standing twenty-four hours deposited a mass of very minute greenish-yellow crystals. These were filtered off, washed with cold water, and then drained by the filter-pump. The drained mass was greenish yellow, and packed into a gummy solid. The filtrate on evaporation gave a fresh quantity of the same salt, which is rather soluble in cold, and very easily soluble in hot water. Of this salt,

0.9333 gr. lost by heating over a radiator 0.0398 gr. = 4.27%
0.9333 gr. gave 0.6094 gr. $WO_3 + P_2O_5$ = 65.29%
1.0505 gr. " 0.2413 gr. As_2O_3 with iodine = 22.97%
0.8456 gr. " 0.0472 gr. $P_2O_7Mg_2$ = 3.57%

The analyses correspond fairly well with the formula

$$32\ WO_3 . 14\ As_2O_3 . 3\ P_2O_5 . 10\ K_2O + 28\ aq,$$

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which requires:

		Calc'd.		Found.	
32 WO_3	7424	61.51	88.00	61.72	88.26
14 As_2O_3	2772	22.96		22.97	
3 P_2O_5	426	3.53		3.57	
10 K_2O	944	7.82		7.58	
28 H_2O	504	4.18		4.27	
	12070	100.00			

12 : 2 : 2 : 6 *Sodio-potassic Arsenoso-phospho-tungstate.* — When sodic phospho-tungstate,

$$24\ WO_3 . P_2O_5 . 2\ Na_2O + 27\ aq,$$

in solution, is boiled with arsenous oxide in excess, this last dissolves freely to a colorless or nearly colorless liquid. On adding ammonic chloride no precipitate is formed, but after acidulating with chlorhydric acid a white crystalline precipitate is thrown down. On standing, the supernatant liquid deposits very distinct pale yellow tabular crystals. When potassic bromide is added to the sodic solution, a yellow oil separates after a time, which dries to a pale yellow gummy transparent mass. Of this salt,

0.9284 gr.	lost over a radiator	0.0595 gr.	= 6.41%	
0.9492 gr.	gave	0.0822 gr. As_2O_3 with iodine	= 8.65%	
1.2191 gr.	"	0.1061 gr. " "	= 8.70%	
0.8961 gr.	"	0.0944 gr. $P_2O_7Mg_2$	= 6.74%	P_2O_5
0.8916 gr.	"	0.6458 gr. $P_2O_5 + WO_3$	= 72.43%	
0.8916 gr.	"	0.5064 gr. $PtCl_6K_2$	= 11.03%	K_2O

The formula which best represents the analyses is

$$12\ WO_3 . 2\ As_2O_3 . 2\ P_2O_5 . 5\ K_2O . Na_2O + 15\ aq,$$

which requires:

		Calc'd.	Found.	
12 WO_3	2784	65.24	65.69	
2 As_2O_3	396	9.28	8.65	8.70
2 P_2O_5	284	6.65	6.74	
5 K_2O	472	11.06	11.03	
Na_2O	62	1.45	1.48	
15 H_2O	270	6.32	6.41	
	4268	100.00		

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The arsenous oxide is too low, but the sum of the arsenous and tungstic oxides, as well as the percentages of the other constituents of the salts, agree well with the formula.

60 : 1 : 4 : 7 *Potassic Arsenoso-phospho-tungstate.* — When a solution of potassic phosphate is poured into one of sodic arsenoso-tungstate as prepared by boiling arsenous oxide with 12 : 5 sodic tungstate, no precipitate is formed; but on adding chlorhydric acid the liquid becomes yellow, and, after standing, deposits beautiful pale yellow crystals. For analysis these were washed with cold water and dried on woollen paper. The salt is soluble in hot water, but appears to be decomposed by solution. In this salt,

1.2498 gr. gave 0.0671 gr. $P_2O_7Mg_2$ = 3.43% P_2O_5
1.2587 gr. " 0.0151 gr. As_2O_3 by iodine = 1.20%
1.0348 gr. " 0.9192 gr. $WO_3 + P_2O_5$ = 88.81%
1.3143 gr. lost over a radiator 0.0787 gr. = 5.99% water.

The analyses correspond closely to the formula

$$60\ WO_3 . As_2O_3 . 4\ P_2O_5 . 7\ K_2O + 55\ aq,$$

which may also be written

$$60\ WO_3 . 2\ AsO_3H_3 . 4\ P_2O_5 . 7\ K_2O + 52\ aq.$$

The formula requires:

		Calc'd.	Found.
60 WO_3	13920	85.21	85.38
4 P_2O_5	568	3.48	3.43
As_2O_3	198	1.21	1.20
7 K_2O	661	4.04	4.00 (diff.)
55 H_2O	990	6.06	5.99
	16337	100.00	

It is of course very possible that this may be a double salt, but there are at present no data upon which we can base a rational distribution of the components.

ARSENOSO-ARSENIO-TUNGSTATES.

The salts which belong to this group are formed under the same conditions as the corresponding arsenoso-phospho-tungstates. They are in many cases highly crystalline and well defined, and appear to be very numerous.

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Analytical Methods. — Arsenic acid may be directly determined in the soluble salts of this series by means of magnesia-mixture, but it is best to redissolve the precipitated ammonio-magnesic arsenate in chlorhydric acid, and precipitate a second time by ammonia. Arsenous oxide may be determined by titrition with iodine after adding an excess of an alkaline dicarbonate. As a check upon the determination of the two oxides of arsenic, it is well to oxidize a portion of the salt directly by means of nitric acid, and then determine the total arsenic oxide by means of magnesia-mixture. A further check may also be obtained by reducing the arsenic oxide by boiling with sulphurous acid, and then titrating the total arsenous oxide by means of iodine. In solutions from which the arsenic has been completely removed as As_2S_3, tungsten can be determined by means of mercurous nitrate, provided that no chlorhydric acid or chloride is present.

21 : 1 : 4 : 10 *Potassic Arsenoso-phospho-tungstate.* — When potassic bromide is added to a solution of arsenoso-tungstate of soda, and a solution of potassic arsenate, AsO_4K_2H, is then poured into the clear filtrate, a white crystalline precipitate is formed. This salt requires a very large quantity of hot water for solution. Baric chloride boiled with it gives a well-defined flocky-crystalline salt. Argentic nitrate gives a similar salt, but this has a faint tinge of fawn-color, perhaps due to the presence of a trace of potassic arsenate not completely removed by washing. Mercurous nitrate gives on boiling a clear yellow flocky-crystalline salt. In the potassic salt,

1.9985 gr. gave 0.3468 gr. $As_2O_7Mg_2$ = 12.36% As_2O_5
2.0085 gr. " 0.0527 gr. As_2O_3 by iodine = 2.62% As_2O_3

After complete oxidation by nitric acid,

1.5004 gr. gave 0.3162 gr. $As_2O_7Mg_2$ = 15.63% As_2O_5
1.9684 gr. " 1.2935 gr. WO_3 = 65.72%
1.5825 gr. " 1.0346 gr. " = 65.37%
1.3890 gr. " 0.9382 gr. $PtCl_6K_2$ = 13.09% K_2O
1.5765 gr. lost over a radiator 0.0955 gr. = 6.06%

The analyses lead to the formula

$$21\ WO_3 . As_2O_3 . 4\ As_2O_5 . 10\ K_2O + 26\ aq,$$

which requires :

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		Calc'd.	Found.	
21 WO_3	4872	65.86	65.72	65.37
As_2O_3	198	2.68	2.62	
4 P_2O_5	920	12.43	12.36	
10 K_2O	940	12.70	13.09	
26 H_2O	468	6.33	6.06	6.39 (diff.)
	7398	100.00		

Of course, in this salt, as in the arsenoso-phospho-tungstates described, arsenic may be supposed to be in the form of $\{H.AsO.(OH)_2\}$ either wholly or partially.

Classes of antimonoso-arsenio-tungstates, antimonoso-antimonio-tungstates, and arsenoso-antimonio-tungstates, appear also to exist and to be formed by processes exactly analogous to those described in the cases of the compounds containing two oxides respectively of the forms R_2O_3 and R'_2O_5, united with tungstic oxide.

ANTIMONOSO-PHOSPHO-TUNGSTATES.

These salts are formed under the same conditions as the corresponding arsenoso-phospho-tungstates, and the methods of analysis to be employed are the same.

22 : 6 : 5 : 12 *Potassic Antimonoso-phospho-tungstate.* — When a solution of potassic phosphate is poured into a hot solution of sodic antimonoso-tungstate as obtained by dissolving SbOCl in 10 : 4 sodic tungstate, a very pale yellow highly crystalline salt is at once formed. This is nearly insoluble in both hot and cold water. The portion analyzed was filtered off, washed upon the filter-pump with cold water, drained, and dried upon woollen paper. The salt, like many others which I have described, could not be recrystallized, but I give the results of the analyses for what they may prove to be worth. They certainly, I think, establish the existence of the series. In this salt,

{ 0.7776 gr. gave 0.6142 gr. oxides = 78.99%
{ 0.7776 gr. " 0.4763 gr. $PtCl_6K_2$ = 11.90%
1.0323 gr. " with iodine 0.1594 gr. Sb_2O_3 = 15.44%
0.9716 gr. " " 0.1509 gr. " = 15.53%
1.2300 gr. " 0.1805 gr. $P_2O_7Mg_2$ = 9.20% P_2O_5
1.2430 gr. " 0.1821 gr. " = 9.37% "

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The analyses lead to the formula:

$$22\ WO_3\ .\ 5\ Sb_2O_3\ .\ 6\ P_2O_5\ .\ 12\ K_2O + 48\ aq,$$

which requires:

		Calc'd.	Found.	
22 WO_3	5104	54.34	54.23	
6 P_2O_5	852	9.07	9.20	9.37
5 Sb_2O_3	1440	15.33	15.44	15.53
12 K_2O	1133	12.07	11.90	
48 H_2O	864	9.19	9.13 (diff.)	
	9393	100.00		

ANTIMONIO-TUNGSTATES.

As already stated, these compounds are formed by the direct oxidation of antimonoso-tungstates, one molecule of oxygen being absorbed. I shall hereafter show that, in place of oxygen, platinous chloride and other divalent compounds may serve as complex replacing molecules. Antimonio-tungstates are also formed when antimonic hydrate in excess is boiled with an acid tungstate, and when tungstic teroxide is digested or boiled with an alkaline antimonate. The salts of this series are, as a whole, not so well defined as the phospho-tungstates, vanadio-tungstates, and arsenio-tungstates, and are much more difficult to prepare in a state of purity.

Analytical Methods. — These are essentially the same as those which I have given in the case of the antimonoso-tungstates. Antimonic and tungstic oxides may be precipitated together by mercurous nitrate and mercuric oxide. In the ignited precipitate it must be assumed that the antimony is in the form of tetroxide, Sb_2O_4, and the proper correction applied, after a special determination of the antimony, as sulphide or as metal.

6 : 2 *Antimonio-tungstate of Potassium.* — This salt was prepared by boiling potassic di-antimonate for a long time with a solution of 12 : 5 acid potassic tungstate. After filtration from a small quantity of the antimonate in excess, the filtrate, on standing twenty-four hours, deposited colorless granular crystals, which were washed with cold water and dried upon woollen paper. The salt was not very soluble in water ; the crystals were soft and packed together between the fingers. In this salt,

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1.0881 gr. lost on ignition with WO_4Na_2 0.1076 gr. = 9.89 %
1.3566 gr. " " " 0.1379 gr. = 10.16 %
1.4636 gr. gave 1.1178 gr. $WO_3 + Sb_2O_4$ = 76.36 %
1.3425 gr. " with KCy 0.2529 gr. Sb = 25.12 % Sb_2O_5
0.9095 gr. " " 0.1700 gr. Sb = 24.92 % "
0.8710 gr. " 0.5011 gr. $PtCl_6K_2$ = 11.16 % K_2O

The analyses lead to the formula

$$12\ WO_3\ .\ 4\ Sb_2O_5\ .\ 6\ K_2O + 25\ aq,$$

which requires:

		Calc'd.	Found.	
12 WO_3	2784	54.81	55.04	
4 Sb_2O_5	1280	25.19	25.12	24.92
6 K_2O	566	11.14	11.16	
25 H_2O	450	8.86	8.91	8.64
	5080	100.00		

In calculating the results of the analysis for comparison, I have assumed that, in the ignition with the sodic tungstate to determine the water, antimonic oxide is reduced to the tetroxide Sb_2O_4; a correction must therefore be applied to the apparent loss. This amounts to one twentieth of the percentage of antimonic pentoxide, and is of course to be deducted from the total loss. Chemists usually admit the existence of three classes of antimonates, corresponding respectively to metaphosphates, pyrophosphates, and orthophosphates, and formulas to support this view have been somewhat arbitrarily assigned to known compounds. If we suppose that the antimonio-tungstate above described contains metantimonic oxide, we may write the formula as we shall write those of corresponding metaphospho-tungstates,

$$12\ WO_3\ .\ 8\ SbO_3K\ .\ 2\ K_2O + 25\ aq.$$

A solution of this salt gives white crystalline precipitates with baric chloride, argentic nitrate, and cupric sulphate, and a yellow flocky-crystalline precipitate with mercurous nitrate.

ANTIMONIO-MOLYBDATES.

Salts belonging to this group are formed when freshly prepared antimonic hydrate is boiled with an acid molybdate in solution, when antimonic pentachloride in solution in chlorhydric acid is poured into a solution of an alkaline molybdate in small quantities at a time,

and when molybdic oxide is digested with a solution of an alkaline antimonate.

Analytical Methods. — The separation of antimony from molybdenum cannot be effected by sulphydric acid, because molybdic sulphide is always precipitated in greater or less quantity, even when phosphoric acid is present in the solution. The only method which I have been able to devise consists in fusing the salt to be analyzed or the mixture of oxides with potassic cyanide, as in the case of the separation of antimony from tungsten. In this case also it is always advisable, and sometimes necessary, to add a sufficient quantity of an alkaline carbonate to form a mixture of neutral molybdate and antimonate, as suggested by Mr. Herman Schmidt. With proper care the two oxides may be precipitated together by mercurous nitrate and mercuric oxide, and ignited without sensible loss of molybdic oxide; but there is then always a certain amount of reduced metallic antimony present, and on the whole the method is not to be recommended.

7 : 3 : 5 *Ammonic Antimonio-molybdate.* — Antimonic hydrate dissolves readily on boiling with a strong solution of 14 : 6 ammonic molybdate. The hydrate should be in excess, and should be added in small portions at a time, until, after long boiling, a part remains undissolved. After standing twenty-four hours, beautiful colorless crystals are deposited in quantity. These have a nacreous lustre, and are readily soluble in hot water. In this salt,

1.0647 gr. lost on ignition with WO_4Na_2 0.2052 gr. = 19.55 %
1.2234 gr. gave 0.2418 gr. NH_4Cl = 9.60 % $(NH_4)_2O$
0.9576 gr. " with KCy 0.3321 gr. Sb = 46.24 % Sb_2O_5.

The analyses correspond with the formula

$$7\ MoO_3 . 4\ Sb_2O_5 . 5\ (NH_4)_2O + 12\ aq,$$

which requires:

		Calc'd.	Found.
7 MoO_3	1008	36.47	36.52
4 Sb_2O_5	1280	46.31	46.24
5 $(NH_4)_2O$	260	9.40	9.60
12 H_2O	216	7.82	7.64
	2764	100.00	

The formula may also be written

$$7\ MoO_3 . 8\ SbO_3NH_4 . (NH_4)_2O + 12\ aq.$$

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The solution of this salt gives with manganous sulphate after a time a fine canary-yellow crystalline precipitate. The ammonium salt appears to be decomposed by evaporation to dryness, or perhaps by the act of solution. The dry residue, on addition of water, leaves a white insoluble crystalline substance.

The existence of classes of vanadio-phospho-tungstates and vanadio-phospho-molybdates has already been proved. These may be embraced under the general formulas

$$m\ V_2O_5 \cdot n\ P_2O_5 \cdot p\ WO_3, \qquad m'\ V_2O_5 \cdot n'\ P_2O_5 \cdot p'\ MoO_3.$$

I believe that I am fully justified, though from qualitative experiments only, in maintaining that the formula

$$m\ R_2O_5 \cdot n\ R'_2O_5 \cdot p\ R''_2O_3$$

is general, and that R_2O_5 and R'_2O_5 may represent any two pentoxides, at least of the series P_2O_5 . V_2O_5 . As_2O_5 and Sb_2O_5.

PYROPHOSPHO-TUNGSTATES.

The phospho-tungstates and phospho-molybdates which have hitherto been described must be regarded as containing phosphoric oxide in the modification in which it exists in the class of tribasic or ortho phosphates. This appears to be clearly shown, first, by the synthesis of these compounds from orthophosphoric acid and orthophosphates and the acid tungstates and molybdates; and, secondly, from the fact that in all cases, after the addition of an excess of ammonia, magnesia-mixture at once throws down the characteristic ammonio-magnesic orthophosphate. I shall now show that the other modifications of phosphoric oxide or acid enter as such into similar compounds, so that we have perfectly well defined groups of pyrophospho-tungstates, metaphospho-tungstates, etc., and corresponding compounds containing molybdenum; and that, in the compounds so formed, the various modifications of phosphoric oxide preserve as it were their individuality. I shall further render it at least probable that there are groups — of phospho-tungstates for instance — in which two different modifications of phosphoric oxide may exist, each preserving its own characteristic properties. I do not now assert that in each of the complex groups which I have described orthophosphoric acid may be replaced by some other modification. That remains for experimental investigation. It is at least clear that the field already opened for study is one of

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practically unlimited extent, as even an elementary application of the algebraical theory of permutations and combinations will show.

Pyrophospho-tungstates are formed when tungstic hydrate or tungstic oxide which has not been ignited is boiled with an alkaline pyrophosphate. The oxide readily dissolves, usually forming a yellow liquid. It is best to employ sodic pyrophosphate, as this gives a much more soluble salt, but the pyrophosphate must be specially prepared in the laboratory, and the tungstic oxide should be in excess. Neutral salts of the heavy metals usually give precipitates in solutions of the alkaline pyrophospho-tungstates; these precipitates are not necessarily salts of the same group, but are very often at least either pyrophosphates of the metallic bases or double pyrophosphates of the metal and of sodium or potassium.

Analytical Methods. — These are the same as those which I have employed in the case of the orthophospho-tungstates, only in the determination of the phosphoric oxide it is necessary to evaporate the salt two or three times in succession to dryness with an excess of chlorhydric acid, so as to convert the phosphoric acid present completely into the ortho or tribasic form. In the absence of any standard of comparison, it is necessary to speak with much hesitation, but it has always appeared to me that in these salts — in other words, in the presence of tungstic oxide — the conversion of pyrophosphoric acid into orthophosphoric acid is more difficult, or at least takes place more slowly, than in the case of the ordinary pyrophosphates. Tungstic and phosphoric oxides may in these compounds also be precipitated together by mercurous nitrate and mercuric oxide.

22 : 3 : 6 *Ammonio-sodic Pyrophospho-tungstate.* — A boiling solution of sodic pyrophosphate readily dissolves tungstic oxide as prepared by the action of chlorhydric or nitric acid upon calcic tungstate, but not ignited. The filtrate has a dull yellow color, and gives with a strong solution of ammonic chloride an abundant white crystalline precipitate, which cannot be purified by recrystallization, but which may be well washed upon the filter-pump with cold water, in which it is soluble to a very small extent. Hot water in large excess dissolves it, but even cold ammonia water dissolves it with much difficulty. When boiled for a long time with a solution of mercurous nitrate, the salt gives at first a white and finally a yellow mercurous salt. Argentic nitrate in solution gives at first with the salt extremely minute talcose scales, but on boiling for some time the whole dissolves to a clear liquid. When the salt is boiled with a solution of baric chloride, a flocky-crystalline white baric salt is formed. Cupric sulphate on boil-

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ing dissolves the pyrophospho-tungstate, but on cooling a pale green crystalline body separates, which does not contain tungsten. The salt, precipitated by ammonic chloride as above, after washing with cold water and drying upon woollen paper, was analyzed:

0.6626 gr. lost on ignition 0.1060 gr. = 16.00 NH_3 and H_2O
0.9866 gr. gave 0.2479 gr. $P_2O_7Mg_2$ = 16.07 % P_2O_5
0.5488 gr. " 0.0499 gr. $(NH_4)_2O$ = 9.09 %
0.8188 gr. " 0.6504 gr. oxides = 79.46 % WO_3 and P_2O_5.

In determining the phosphoric oxide, the salt was several times in succession evaporated to dryness with nitric acid.

The analyses agree with the formula

$$22\ WO_3 . 3\ \{P_2O_7Na_4\}\ 6\ \{P_2O_7(NH_4)_4\}\ 2\ (NH_4)_2O + 31\ aq,$$

which requires:

		Calc'd.	Found.
22 WO_3	5104	63.48	63.39
9 P_2O_5	1278	15.90	16.07
6 Na_2O	372	4.63	4.54 (diff.)
14 $(NH_4)_2O$	728	9.06	9.09
31 H_2O	558	6.93	6.91
	8040	100.00	

As already stated, the salt is dissolved by a large excess of hot water to a clear colorless solution. Cupric sulphate gives in this solution a pale blue crystalline precipitate of a pyrophosphate free from tungstic oxide. Argentic nitrate and baric chloride give white flocky-crystalline precipitates. Either, therefore, the salt is decomposed by solution or by the action of cupric sulphate.

22 : 9 : 18 *Potassic Pyrophospho-tungstate.* — When potassic bromide and acetic acid are added to the saturated solution of tungstic oxide in sodic pyrophosphate, a white granular fine-grained crystalline precipitate very slightly soluble in cold water is formed at once. For analysis the salt was washed upon the filter-pump with cold water, and dried on woollen paper. In this salt,

0.9440 gr. gave 0.6717 gr. oxides = 71.15% WO_3 and P_2O_5
1.3647 gr. " 0.9721 gr. " = 71.23% " "
0.9070 gr. " 0.2015 gr. $P_2O_7Mg_2$ = 14.21% P_2O_5
0.9817 gr. lost 0.0960 gr. H_2O = 9.78%

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The phosphoric oxide was determined as before by evaporation with nitric acid to convert the pyrophosphoric into orthophosphoric acid.

The analyses correspond to the formula

$$22\ WO_3 . 9\ P_2O_7K_4 + 49\ aq,$$

which requires:

		Calc'd.	Found.	
22 WO_3	5104	56.94	56.94	57.02
9 P_2O_5	1278	14.26	14.21	
18 K_2O	1699	18.96	19.07	
49 H_2O	882	9.84	9.78	
	8963	100.00		

22 : 9 : 13 *Potassic Pyrophospho-tungstate.* — This salt was obtained by boiling tungstic oxide for some time with potassic pyrophosphate. After filtration and standing a white crystalline salt separated, which was well drained on the filter-pump, and then washed with cold water in which it is but slightly soluble. In much boiling water it dissolves on boiling to a clear liquid. The solution gives a white crystalline precipitate with argentic nitrate, — no precipitate at first with cupric sulphate. On boiling, a very pale blue crystalline salt separates, which does not contain tungsten, and is either a cupric pyrophosphate or a double salt of potassium and copper. The solution of the pyrophospho-tungstate gives a dense white distinctly crystalline precipitate with mercurous nitrate, and a turbid solution with baric chloride yielding on boiling a white feathery crystalline salt. No precipitate is formed with manganous sulphate, but after a short time the solution becomes turbid. In this salt,

1.6112 gr. gave 1.2119 gr. oxides = 75.22%
1.9796 gr. " 1.4894 gr. " = 75.23%
1.6421 gr. " 0.3862 gr. $P_2O_7Mg_2$ = 15.06%
1.2433 gr. lost by direct ignition 0.1299 gr. = 10.45%

The analyses agree closely with the formula

$$22\ WO_3 . 6\ P_2O_7K_4 . 3\ P_2O_7H_4 . K_2O . H_2O + 42\ aq,$$

so that the type is, as in other cases,

$$22\ WO_3 . 9\ P_2O_7H_4 . 2\ R_2O.$$

The formula requires:

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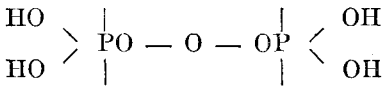
		Calc'd.	Found.
22 WO_3	5104	60.11	60.17 60.18
9 P_2O_5	1278	15.05	15.05
13 K_2O	1227	14.45	14.32 (diff.)
49 H_2O	882	10.39	10.45
	8491	100.00	

All the compounds of this group which I have obtained belong, as will be seen, to the same type which contains the frequently recurring chemical mass of twenty-two molecules of tungstic oxide, united to nine molecules of pyrophosphoric acid or a pyrophosphate, together with a certain amount of base over and above that required to saturate the phosphoric oxide. We may represent this group provisionally by a structural formula containing *nine* groups of the form:



Further investigation will doubtless show that there are other series of pyrophospho-tungstates and analogous pyrophospho-molybdates. It is especially desirable to study the compounds which remain in solution after the precipitation of part of the pyrophosphoric oxide by means of cupric sulphate.

It may here be remarked, that Wallroth * has described a series of pyrophosphates which contain *nine* molecules of P_2O_7, united in each case to thirty-six atoms of metal. Thus we have

$$Ca_{10}\ Na_{16}\ (P_2O_7)_9$$
$$Mg_{10}\ Na_{16}\ (P_2O_7)_9$$
$$Co_{10}\ Na_{16}\ (P_2O_7)_9$$
$$Ni_{10}\ Na_{16}\ (P_2O_7)_9.$$

It would therefore appear that similar complex molecules enter directly into combination with twenty-two molecules of tungstic oxide, but that the complexity is not necessarily due to a determining action on the part of the latter.

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* Bull. de la Soc. Chimique, [2,] xxxix. 316.

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MONOMETAPHOSPHO-TUNGSTATES.

In preparing the salts of this series I have employed ordinary glacial phosphoric acid, which, according to Brescius,* contains about 50% of sodic metaphosphate, and which may be regarded as a mixture of sodic metaphosphate and metaphosphoric acid. I have assumed that the acid is here in the form of monometaphosphoric acid, although upon this point the evidence is still insufficient. As the relations of metaphosphoric acid to indicators of various kinds have not hitherto been studied, the following brief note may be of interest. A solution of glacial phosphoric acid is neutral to tropæolin. The same solution required for equal volumes with purpurin 23 cc. sodic hydrate solution; with hæmatoxylin, 14 cc.; and with alizarin, 12.5 cc. No definite end reaction could be obtained with phenol-phthalein, methyl-orange, or rosolic acid.

Monometaphospho-tungstates are formed by the direct action of the acid upon acid tungstates. They are, frequently at least, gummy uncrystalline bodies. When crystalline the crystals are usually soft, and pack together readily. The salts of the alkaline earths are usually more or less distinctly crystalline. Those of the heavy metallic oxides are often pasty, and sometimes oily. They are not very readily converted into orthophospho-tungstates, and in this respect they seem to differ materially from the corresponding metaphospho-molybdates.

Analytical Methods. — In these salts tungstic and metaphosphoric oxides may be precipitated together by mercurous nitrate and mercuric oxide. Metaphosphoric acid may be converted into orthophosphoric acid by dissolving the salt in the least possible quantity of water, adding strong sulphuric acid, evaporating the solution nearly to dryness, and repeating this process several times. This method is very much better than fusion with alkaline carbonates, which effects the transformation of metaphosphoric acid in a very imperfect manner. I believe that I can assert with entire confidence, that in the class of monometaphospho-tungstates the conversion of the metaphosphoric into orthophosphoric acid is much more difficult than in the metaphosphates. The precipitation of the orthophosphoric acid by magnesia-mixture must of course be repeated twice.

24 : 2 : 3 *Potassic Monometaphospho-tungstate.* — When a cold freshly prepared solution of glacial phosphoric acid is digested with 10 : 4 potassic tungstate, part of this salt dissolves, while the undissolved

* Zeitschrift für analytische Chemie, vi. 187.

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portion changes its character, and is converted into a soft crystalline, very slightly soluble mass. This may be filtered off, and washed with cold water. In this salt,

1.5236 gr. lost on ignition 0.0857 gr. = 5.63%
1.5236 gr. gave 0.0517 gr. $P_2O_7Mg_2$ = 1.96% P_2O_5
0.9934 gr. " 0.0303 gr. " = 2.17% "
1.0686 gr. " 0.0352 gr. " = 2.11% "
1.1490 gr. " 1.0171 gr. oxides = 88.52%
1.1490 gr. " 0.3327 gr. $PtCl_6K_2$ = 5.70% K_2O

The analyses correspond very well to the formula

$$24\ WO_3 . 2\ \{PO_3K\}\ 3\ K_2O + 20\ aq,$$

which requires:

		Calc'd.	Found.		
24 WO_3	5568	86.36		86.38	
P_2O_5	142	2.21	2.11	2.17	1.96
4 K_2O	376	5.84	5.70		5.85 (diff.)
20 H_2O	360	5.59		5.63	
	6446	100.00			

The filtrate from the 24 : 2 salt, on standing, deposits a white crystalline salt, which, when thrown on a filter and washed with cold water, presents a colorless gummy mass. Of this salt,

0.6183 gr. gave 0.0307 gr. $P_2O_7Mg_2$ = 3.17% P_2O_5
0.8173 gr. " 0.6844 gr. oxides = 83.72%
0.8173 gr. lost on ignition 0.0607 gr. = 7.43%

From an oversight, the potassic oxide was not determined in this salt, which may be either

$$16\ WO_3 . 2\ \{PO_3K\}\ 2\ K_2O . 2\ Na_2O + 20\ aq,$$

or

$$16\ WO_3 . 2\ \{PO_3K\}\ 5\ Na_2O + 20\ aq.$$

The formulas require, respectively,

		Calc'd.		Found.	Calc'd.			
16 WO_3	3712	80.34		80.56	80.38		3712	16 WO_3
P_2O_5	142	3.07		3.17	3.07		142	P_2O_5
3 K_2O	283	6.12	8.80	8.87	2.04	8.76	94	K_2O
2 Na_2O	124	2.68			6.72		310	5 Na_2O
20 H_2O	360	7.79		7.40	7.79		360	20 H_2O
	4621	100.00			100.00		4618	

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18 : 1 : 2 *Ammonic Monometaphospho-tungstate.* — When 12 : 5 ammonic tungstate is boiled with a solution of glacial phosphoric acid, a white crystalline mass remains undissolved, very different in appearance from the ammonic tungstate employed. This salt requires a large quantity of boiling water for solution, but is only slightly soluble in cold water. For analysis, it was thoroughly drained upon the filter-pump, and then washed with cold water. Of this salt,

1.6896 gr. lost by ignition with WO_4Na_2 0.1082 gr. = 6.40%
1.5026 gr. gave 0.0745 gr. $P_2O_7Mg_2$ = 3.17% P_2O_5
1.4267 gr. " 0.0316 gr. $(NH_4)_2O$ = 2.21%

The analyses correspond to the formula

$$18\ WO_3 . 2\ \{PO_3NH_4\} . (NH_4)_2O + 11\ aq,$$

which requires:

		Calc'd.	Found.
18 WO_3	4176	90.39	90.43
P_2O_5	142	3.08	3.17
2 $(NH_4)_2O$	104	2.25	2.21
11 H_2O	198	4.28	4.19
	4620	100.00	

The filtrate from this salt gives on evaporation a thick colorless syrup, in which white crystals — perhaps of the salt above described — were suspended. It will be seen that the action of PO_3H upon 12 : 5 ammonic tungstate is essentially the same as upon the 10 : 4 potassic salt, and that in each case at least one crystalline and one gummy salt are formed.

The analyses given are sufficient to establish the existence of three classes of monometaphospho-tungstates. My work on this subject is to be regarded merely as preliminary, and is intended to direct the attention of other chemists to this class of salts. In another paper I shall give the results of a more detailed study of the various metaphospho-tungstates. Fleitmann and Henneberg have described five series of metaphosphates; in addition to these, there remain to be studied, in their relation to tungstic and molybdic oxides, the two series of tetraphosphates, $P_4O_7 . 6\ RO$, and dekaphosphates, $P_{10}O_{19} . 12\ RO$, discovered by the same chemists, as well as the new group of salts described by Salzer,* which may be called hypophosphates.

* Pharmaceutische Zeitung, Bunzlau, 1881. Ann. der Chemie, ccxi. 1.

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ORTHOMETAPHOSPHO-TUNGSTATES.

A single salt of this series will be sufficient to establish the existence of compounds into which two different modifications of phosphoric acid enter, to a certain extent at least preserving their peculiar characteristics.

22 : 6 : 11 : 7 *Potassio-sodic Orthometaphospho-tungstate.* — When 24 : 1 sodic phospho-tungstate is boiled with a solution of sodic monometaphosphate, PO_3Na, the salt dissolves readily to a clear liquid. Potassic bromide gives a white precipitate in this solution. After filtering and washing with cold water, a white gelatinous mass remains upon the filter, but slightly soluble in water. Of this salt,

1.2008 gr. gave 0.8728 gr. oxides = 72.68%
1.5959 gr. " 0.1611 gr. " = 72.76%
1.3558 gr. " 0.2220 gr. $P_2O_7Mg_2$ = 10.47% P_2O_5
0.8822 gr. " 0.5774 gr. $PtCl_6K_2$ = 12.70% K_2O
1.4517 gr. lost on ignition with WO_4Na_2 0.1349 gr. = 9.29%

The analyses correspond with the formula

$$22\ WO_3\ .\ 6\ P_2O_5\ .\ 11\ K_2O\ .\ 7\ Na_2O + 42\ aq,$$

which requires:

		Calc'd.	Found.
22 WO_3	5104	62.36	62.25
6 P_2O_5	852	10.41	10.47
11 K_2O	1038	12.68	12.70
7 Na_2O	434	5.31	5.29
42 H_2O	756	9.24	9.29
	8184	100.00	

The solution of this salt in chlorhydric acid gives, with magnesia-mixture and ammonia, a precipitate which appears to contain ammonio-magnesic phosphate and magnesic metaphosphate. It is of course possible that a portion of the metaphosphoric acid may have been converted into orthophosphoric acid by the act of solution in chlorhydric acid. I know of no method by which really reliable determinations, either qualitative or quantitative, can be made in compounds of this kind. In the analysis above, the salt was evaporated several times with strong sulphuric acid, and the phosphoric acid then determined with magnesia-mixture. The total quantity of base in the salt

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is exactly sufficient to saturate six molecules of orthophosphoric acid, but the salt certainly contains at least a part of the phosphorus as metaphosphoric oxide. We may perhaps assume that the two modifications are equally divided between the bases, and the formula may then be written

$$22\ WO_3 . 3\ (P_2O_5 . 3\ K_2O) . 6\ PO_3Na . 2\ K_2O . 4\ Na_2O + 42\ aq.$$

The subject of course requires further investigation.

MONOMETAPHOSPHO-MOLYBDATES.

The salts belonging to this series appear also to belong to two different classes, which may be simply distinguished as crystalline and gummy salts. Both these classes are readily converted by acids into orthophospho-molybdates. Up to the present time I have made only a preliminary study of these compounds.

10 : 2 : 5 *Ammonic Monometaphospho-molybdate.* — When glacial phosphoric acid is neutralized with ammonia, and the solution is mixed with one of 14 : 6 ammonic molybdate, no precipitate is formed, but on evaporation a thick, nearly colorless gummy mass is formed. On standing for some time, this is almost completely converted into a crystalline mass. This may be drained, redissolved in water, in which it is very soluble, and recrystallized several times from very concentrated solutions. It then presents very beautiful, perfectly colorless, flat tabular crystals. The solution gives at once, with nitric acid, a precipitate of yellow orthophospho-molybdate; with magnesia-mixture and ammonia, a precipitate very different from ammonio-magnesic orthophosphate. Argentic nitrate gives a flocky-crystalline precipitate; baric and thallous nitrates give beautiful white feathery-crystalline salts; mercurous nitrate gives a pale flocky-crystalline precipitate, while cuprous sulphate forms none. Of this salt,

1.4314 gr. gave 0.3002 gr. $P_2O_7Mg_2$ = 13.41% P_2O_5
0.8385 gr. " 0.1022 gr. $(NH_4)_2O$ = 12.19%
1.4016 gr. lost 0.2776 gr. = 19.81%

The analyses agree with the formula

$$10\ MoO_3 . 2\ P_2O_5 . 5\ (NH_4)_2O + 9\ aq,$$

which requires:

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		Calc'd.		Found.	
10 Mo_2O_3	1440	67.10	80.33	66.78	80.19
2 P_2O_5	284	13.23		13.41	
5 $(NH_4)_2O$	260	12.12		12.19	
9 H_2O	162	7.55		7.62	
	2146	100.00			

The formula may be more advantageously written

$$10\ MoO_3\ .\ 4\ \{PO_3NH_4\}\ .\ 3\ (NH_4)_2O + 9\ aq.$$

Empirically, this salt has, except as regards water of crystallization, the same formula as the acid 10 : 2 orthophospho-molybdate, which I have already described.

HEXAMETAPHOSPHO-MOLYBDATES.

The single salt of this series which I have thus far obtained will serve as an example, and I hope as an incentive to further study.

14 : 3 : 4 *Baric Hexametaphospho-molybdate.* — Sodic hexametaphosphate, obtained by heating the so-called microcosmic salt until a clear colorless glass is obtained, gives a white colorless crystalline salt with baric chloride, which, after washing with cold water, readily dissolves in an excess of a solution of 14 : 6 ammonic molybdate. After a short time the clear filtered solution deposits an abundance of beautiful colorless acicular crystals. This salt cannot be perfectly decomposed by boiling with a solution of mercurous nitrate. Nitric acid dissolves it to a turbid liquid, with formation of a yellow powder. After boiling with the acid, ammonic molybdate gives the characteristic yellow crystalline precipitate, indicating the presence of orthophosphoric acid. Of this salt,

1.0140 gr. lost on ignition with WO_4Na_2 0.2463 gr. = 24.31%
1.8970 gr. gave 0.4286 gr. SO_4Ba = 14.84% BaO
2.0403 gr. " 0.3454 gr. $P_2O_7Mg_2$ = 10.83% P_2O_5.

The formula appears to be

$$14\ MoO_3\ .\ 3\ P_2O_5\ .\ 4\ BaO + 55\ aq,$$

which requires:

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		Calc'd.	Found.
14 MoO_3	2016	49.86	50.02
3 P_2O_5	426	10.53	10.83
4 BaO	612	15.13	14.84
55 H_2O	990	24.48	24.31
	4044	100.00	

I give this formula with much reserve, and only as probably correct. To express the presence of hexametaphosphoric oxide, it may be written

$$14\ MoO_3 \cdot \{Ba_3 \cdot 6\ PO_3\} \cdot BaO + 55\ aq.$$

I shall return to the subject at another time.

STANNO-PHOSPHO-TUNGSTATES.

The vanadico-vanadio-tungstates and vanadico-vanadio-molybdates which I have described furnish instances of compounds embraced under the general formulas

$$m\ RO_3 \cdot n\ R'O_2 \cdot p\ R''_2O_5 \cdot r\ R'''_2O.$$

I shall show that the compounds belonging to this type are very numerous, and frequently very well defined. For the present, it will be sufficient to cite two new series of hitherto undescribed salts, my object being to direct the attention of other chemists to a new field of investigation, and to point out methods of preparation and of analysis which may facilitate their work.

Stanno-phospho-tungstates are formed when the stanno-chlorides of ammonium or of the alkaline metals are mixed in solution with acid alkaline tungstates. They are colorless crystalline salts, so far as studied. As a representative of this series we may take the ammonium salt.

Analytical Methods. — In these salts the three higher oxides may be determined together by precipitation with mercurous nitrate and mercuric oxide, but the ignited oxides should be evaporated once or twice with nitric acid to oxidize any reduced tin. Tin may be separated as metal by fusion with potassic cyanide, and phosphoric oxide may be determined after separating tin with sulphydric acid.

22 : 2 : 1 : 2 *Ammonic Stanno-phospho-tungstate.* — When a solution of stanno-chloride of ammonium is poured into a clear cold solution of

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24 : 1 sodic phospho-tungstate ($24\ WO_3\ .\ P_2O_5\ .\ 2\ Na_2O + 27$ aq), a beautiful white crystalline precipitate is formed at once. This is but slightly soluble in boiling water. By long boiling with baric chloride, argentic nitrate, or mercurous nitrate, the salt gives crystalline compounds, which in the cases of the barium and silver salts are colorless; in that of the mercurous salt, yellow. So far as can be determined without quantitative analyses, there appears to be in these cases only a simple double decomposition. For analysis the ammonium salt was thoroughly washed with cold water on the filter-pump, drained, and dried on woollen paper. Of this salt,

1.3577 gr. lost on ignition with WO_4Na_2	0.0833 gr.	=	6.14 %
1.2921 gr. " " without "	0.0812 gr.	=	6.29 %
1.6822 gr. gave 0.0646 gr. Sn		=	4.88 % SnO_2
1.1596 gr. " 1.0850 gr. oxides		=	93.57 %
1.1826 gr. " 0.0443 gr. $P_2O_7Mg_2$		=	2.39 %
0.9575 gr. " 0.0182 gr $(NH_4)_2O$		=	1.89 %

The analyses correspond well with the formula

$$22\ WO_3\ .\ 2\ SnO_2\ .\ P_2O_5\ .\ 2\ (NH_4)_2O + 15\ aq,$$

which requires:

22 WO_3	5104	86.21	86.30
2 SnO_2	300	5.06	4.88
P_2O_5	142	2.39	2.39
2 $(NH_4)_2O$	104	1.75	1.89
15 H_2O	270	4.59	4.24
	5920	100.00	99.70

STANNO-PHOSPHO-MOLYBDATES.

The salts of this series are formed under precisely the same conditions as the corresponding stanno-phospho-tungstates. It is at least probable that it will be found that the two classes of salts may be formed under other conditions, as, for example, by boiling stannic oxide with phospho-tungstates and phospho-molybdates, or by digesting stanno-tungstates and stanno-molybdates with alkaline phosphates or with phosphoric acid; but I have made no experiments to determine these points.

Analytical Methods. — Tin may be determined in these salts by fusion with potassic cyanide, provided that, as in the case of the sepa-

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ration of antimony from tungsten and from molybdenum, a sufficient quantity of an alkaline carbonate is added to convert all the higher oxides present into neutral salts. Under these circumstances, no insoluble compound of molybdenum is formed, and the tin separates in bright metallic globules. Phosphoric acid may be determined in these salts after separating the whole of the tin and the greater part of the molybdenum by means of sulphydric acid. Molybdic oxide is estimated most advantageously by difference.

16 : 4 : 3 : 3 *Ammonic Stanno-phospho-molybdate.* — When a solution of stanno-chloride of ammonium, $SnCl_6(NH_4)_2$, is poured into a hot solution of acid ammonic phospho-molybdate,

$$10\ MoO_3 \cdot 2\ P_2O_5 \cdot 5\ (NH_4)_2O + 7\ aq,$$

a fine bright yellow crystalline precipitate is formed, which quickly settles and leaves a colorless solution. The salt is almost insoluble, even in boiling water, and may perhaps find an application in the separation and quantitative estimation of tin. On boiling with mercurous nitrate it gives a buff-yellow crystalline mercurous salt. Under the same circumstances cupric sulphate yields yellowish-green crystals, and argentic nitrate a very pale yellow, not distinctly crystalline salt. An excess of ammonia readily decomposes the salt with separation of a white gelatinous mass. Of this salt,

0.8648 gr. gave	0.1023 gr. metallic tin	= 15.19 %	SnO_2
2.3780 gr. "	0.3865 gr. $P_2O_7Mg_2$	= 10.40 %	P_2O_5
1.2021 gr. "	0.2016 gr. "	= 10.73 %	"
1.0130 gr. "	0.3839 gr. $(NH_4)_2O$	= 3.79 %	
1.7170 gr. lost on ignition	0.2793 gr.	= 16.27 %	

The analyses give the formula

$$16\ MoO_3 \cdot 4\ SnO_2 \cdot 3\ P_2O_5 \cdot 3\ (NH_4)_2O + 28\ aq,$$

which requires:

		Calc'd.	Found.	
16 MoO_3	2304	57.75	57.97 (diff.)	
4 SnO_2	600	15.04	15.19	
3 P_2O_5	426	10.67	10.73	10.40
3 $(NH_4)_2O$	156	3.91	3.79	
28 H_2O	504	12.63	12.48	
	3990	100.00		

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ALUMINO-MOLYBDATES.

Heinrich Struve,* in 1854, described a remarkable series of salts, which he regarded simply as double molybdates of the sesquioxides of aluminum, iron, manganese, chromium, and ammonia, potash, or soda. These salts were embraced under two different types, particular aluminic, ferric, and chromic salts, having respectively the formulas

$$Al_2O_3 . 6\ MoO_3 + 3\ (K_2O\ .\ MoO_3) + 20\ aq$$
$$Fe_2O_3 . 6\ MoO_3 + 3\ (K_2O\ .\ 2\ MoO_3) + 20\ aq$$
$$Cr_2O_3 . 6\ MoO_3 + 3\ (Na_2O . 2\ MoO_3) + 21\ aq.$$

The manganic salt, on the other hand, was represented by

$$Mn_2O_3 . 6\ MoO_3 + 5\ (K_2O . 2\ MoO_3) + 12\ aq.$$

Parmentier† has recently added a new term to this series, the type being

$$R_2O_3 . 10\ MoO_3 . 2\ R'_2O + x\ aq.$$

The true character of these compounds could not be understood at the time of their discovery. I find that in solutions of the salts described by Struve, potassium or ammonium may be directly replaced by other metals or by alkaloids, — a fact which was, however, noticed by Struve himself. In addition, — and this is of more importance, — I find that there are series which contain the sesquioxides named with phosphoric and molybdic oxides, so that we have classes of ferro-phospho-molybdates, etc. From my point of view, the compounds in question may be classed under three types, of which the following will serve as representatives: —

Alumino-dodeka-molybdates,	$Al_2O_3 . 12\ MoO_3 . 6\ R_2O$
Ferrico-dodeka-molybdates,	$Fe_2O_3 . 12\ MoO_3 . 6\ R_2O$
Chromico-dodeka-molybdates,	$C_2O_3\ . 12\ MoO_2 . 6\ R_2O$
Manganico-hekkaideka-molybdates,	$Mn_2O_3 . 16\ MoO_3 . 5\ K_2O . H_2O + 11\ aq$
Alumino-deka-molybdates,	$Al_2O_3\ . 10\ MoO_3 . 2\ R_2O$
Ferrico-deka-molybdates,	$Fe_2O_3 . 10\ MoO_3 . 2\ R_2O$
Chromico-deka-molybdates,	$Cr_2O_3\ . 10\ MoO_3 . 2\ R_2O.$

All these classes of salts containing oxides corresponding to chlorides of the type R_2Cl_6 are very much less stable than compounds containing

* Petersburg Acad. Bull., xii. 142. † Comptes Rendus, xcv. 839.

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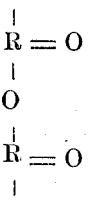
oxides of the types R_2O_5, RO_2, and R_2O_3 (corresponding to chlorides RCl_3). We may assume provisionally that the component



enters into the structural formulas which represent this class of compounds. Struve states that he has obtained similar compounds containing tungsten, but these have not been described.

Klein* has carefully studied four series of boro-tungstates, embraced respectively under the general formulas

$$7\ WO_3 . B_2O_3 . 2\ R_2O$$
$$9\ WO_3 . B_2O_3 . 2\ R_2O$$
$$12\ WO_3 . B_2O_3 . 4\ R_2O$$
$$14\ WO_3 . B_2O_3 . 3\ R_2O.$$

Since boron is the lowest term in the third column of the periodic series, aluminum being the next higher, it would seem probable that the oxides which correspond to still higher terms in the same column will form similar compounds. Chromium, manganese, iron, nickel, and cobalt may be regarded as higher harmonics of aluminum, and at least three of these form analogous series. It still remains to study the relations of the oxides of the cerium and yttrium groups to molybdic and tungstic oxides, since these correspond to chlorides of the type RCl_3, and yet differ in a very marked degree from oxides like As_2O_3, Sb_2O_3, etc. I have made some progress in this investigation and will in another paper give my results in detail.

GENERAL CONCLUSIONS.

The formulas and details which I have given in the present instalment of my work appear to justify the following general conclusions.

1. Vanadic pentoxide unites with phosphoric or arsenic pentoxides in various proportions to form well-defined complex acids. In some, at least, of these, we seem to have series in which vanadic pentoxide

* Bull. de la Société Chim., [2,] xxxvi. 547, xxxvii. 202.

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plays the same part as tungstic or molybdic teroxide, or, in other words, appears to enter the compound as $V_2O_2 . O_3$.

2. Compounds of vanadic pentoxide, vanadic dioxide, and phosphoric or arsenic pentoxide, may be formed, possessing properties analogous to those of the compounds of tungstic or molybdic teroxides with pentoxides and dioxides.

3. The series of oxides P_2O_3, As_2O_3, Sb_2O_3, unite with tungstic and molybdic oxide to form well-defined series of complex acids. In these the ratio of the number of molecules of the oxides of the types R_2O_3 and MO_3 is much lower than in the cases of the compounds which contain orthophosphoric or ortho-arsenic acids.

4. Compounds exist which contain one oxide of the R_2O_3 (or RO_3H_3) and one of the type R'_2O_5 united to tungstic or molybdic oxide, the general formula being

$$m\,MO_3 . n\,R_2O_3 . p\,R'_2O_5 . r\,R''_2O.$$

5. Compounds exist which contain acids of the types RO_2H_3 (hypophosphorous acid, for instance) and R'_2O_5 united to tungstic or molybdic oxides, the general formula being

$$m\,MO_3 . n\,RO_2H_3 . p\,R'_2O_5 . r\,R''_2O.$$

6. Classes of compounds exist which contain oxides of the types RO_2 and R'_2O_5 united to tungstic or molybdic oxides, the general formula being

$$m\,MO_3 . n\,RO_2 . p\,R'_2O_5 . r\,R_2O,$$

where, as in the other general formulas, M represents either tungsten or molybdenum.

7. Compounds exist which contain pyrophosphoric and metaphosphoric acids in place of orthophosphoric acid. So far as it is possible to judge from the salts analyzed, these contain, or at least may contain, phosphoric and tungstic or molybdic oxides in a lower ratio to each other than in the orthophospho-compounds.

8. Complex acids exist which contain two different modifications of phosphoric acid, as, for instance, metaphosphoric and orthophosphoric acids or oxides.

9. The salts described by Struve and by Parmentier establish the existence of a class of complex acids, which contain oxides of the type R_2O_3, corresponding to chlorides of the type R_2Cl_6. The true character of these salts is for the first time recognized.

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Partly for convenience of reference, and partly to show as distinctly as possible the extent and richness of the field of investigation now opened, I have collected all the formulas of the last and present instalments of my work, prefixing the mark † to those which are in my judgment less certainly established.

PHOSPHO-VANADATES.

$P_2O_5 . V_2O_5 . (NH_4)_2O + aq.$
$P_2O_5 . V_2O_5 . 2\ Ag_2O + 5\ aq.$
$P_2O_5 . 2\ V_2O_5 . (NH_4)_2O + 7\ aq.$
$4\ P_2O_5 . 6\ V_2O_5 . 3\ K_2O + 21\ aq.$
$7\ P_2O_5 . 6\ V_2O_5 . 3\ H_2O + 34\ aq.$
$20\ V_2O_5 . P_2O_5 . 3\ H_2O + 56\ aq.$

ARSENIO-VANADATES.

$5\ As_2O_5 . 8\ V_2O_5 . 3\ H_2O + 24\ aq.$
† $7\ As_2O_5 . 6\ V_2O_5 . 3\ H_2O.$

PHOSPHO-VANADICO-VANADATES.

$18\ V_2O_5 . VO_2 . 2\ P_2O_5 . 7\ (NH_4)_2O + 50\ aq.$
† $4\ V_2O_5 . VO_2 . 5\ P_2O_5 . 4\ Na_2O + 37\ aq.$
$12\ P_2O_5 . 12\ VO_2 . 6\ V_2O_5 . 5\ K_2O + 40\ aq.$
$12\ P_2O_5 . 14\ VO_2 . 6\ V_2O_5 . 7\ K_2O + 52\ aq.$
$14\ P_2O_5 . 16\ VO_2 . 6\ V_2O_5 . 7\ (NH_4)_2O + 67\ aq.$
$10\ P_2O_5 . 11\ VO_2 . 5\ V_2O_5 . 5\ (NH_4)_2O + 41\ aq.$

ARSENIO-VANADICO-VANADATES.

$12\ As_2O_5 . 12\ VO_2 . 6\ V_2O_5 . 5\ (NH_4)_2O + 7\ aq.$
$9\ As_2O_5 . 9\ VO_2 . 8\ V_2O_5 . 4\ (NH_4)_2O + 11\ aq.$

VANADICO-VANADATES.

$4\ V_2O_5 . 2\ VO_2 . (NH_4)_2O + 8\ aq.$

HYPOPHOSPHO-MOLYBDATES.

$8\ MoO_3 . 2\ PO_2H_3 . 2\ (NH_4)_2O + 2\ H_2O.$

HYPOPHOSPHO-TUNGSTATES.

$18\ WO_3 . 6\ PO_2H_3 . 4\ K_2O + 7\ aq.$

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PHOSPHOROSO-MOLYBDATES.

$24\ MoO_3 . 4\ PO_3H_3 . 4\ (NH_4)_2O + 17$ aq.
$24\ MoO_3 . 4\ PO_3H_3 . 4\ (NH_4)_2O + 25$ aq.

PHOSPHOROSO-TUNGSTATES.

$22\ WO_3 . 4\ PO_3H_3 . 6\ (NH_4)_2O + 25$ aq.
$32\ WO_3 . 16\ PO_3H_3 . 5\ K_2O + 46$ aq.
$22\ WO_3 . 8\ PO_3H_3 . 2\ Na_2O + 25$ aq.

ARSENOSO-TUNGSTATES.

$18\ WO_3 . 2\ As_2O_3 . 7\ (NH_4)_2O + 18$ aq.
$18\ WO_3 . 2\ As_2O_3 . 8\ BaO + 42$ aq.
$16\ WO_3 . 8\ As_2O_3 . 9\ Na_2O + 65$ aq.

ARSENOSO-MOLYBDATES.

$8\ MoO_3 . 2\ As_2O_3 . 3\ BaO + 13$ aq.
† $12\ MoO_3 . 5\ As_2O_3 . 3\ (NH_4)_2O + 24$ aq.
$6\ MoO_3 . 3\ As_2O_3 . 2\ MnO + 6$ aq.

ANTIMONOSO-TUNGSTATES.

$11\ WO_3 . 3\ Sb_2O_3 . 2\ BaO + 18$ aq.

ANTIMONOSO-MOLYBDATES.

$17\ MoO_3 . 3\ Sb_2O_3 . 6\ (NH_4)_2O + 21$ aq.

PHOSPHOROSO-PHOSPHO-TUNGSTATES.

$24\ WO_3 . P_2O_5 . 2\ PO_3H_3 . 5\ K_2O + 13$ aq.

PHOSPHOROSO-PHOSPHO-MOLYBDATES.

$72\ MoO_3 . 3\ P_2O_5 . 2\ PO_3H_3 . 9\ (NH_4)_2O + 38$ aq.

PHOSPHO-HYPOPHOSPHO-TUNGSTATES.

$26\ WO_3 . 4\ P_2O_5 . 2\ PO_3H_3 . 9\ K_2O . Na_2O + 43$ aq.

ARSENOSO-PHOSPHO-TUNGSTATES.

$32\ WO_3 . 14\ As_2O_3 . 3\ P_2O_5 . 10\ K_2O + 28$ aq.
$12\ WO_3 . 2\ As_2O_3 . 2\ P_2O_5 . 5\ K_2O . Na_2O + 15$ aq.
$60\ WO_3 . As_2O_3 . 4\ P_2O_5 . 7\ K_2O + 55$ aq.

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ARSENOSO-ARSENIO-TUNGSTATES.

† $21\ WO_3 . As_2O_3 . 4\ As_2O_5 . 10\ K_2O + 26$ aq.

ANTIMONOSO-PHOSPHO-TUNGSTATES.

$22\ WO_3 . 5\ Sb_2O_3 . 6\ P_2O_5 . 12\ K_2O + 48$ aq.

VANADIO-MOLYBDATES.

$6\ MoO_3 . V_2O_5 . 2\ (NH_4)_2O + 5$ aq.
$16\ MoO_3 . 2\ V_2O_5 . 5\ BaO + 29$ aq.
$18\ MoO_3 . V_2O_5 . 8\ (NH_4)_2O + 15$ aq.

VANADIO-TUNGSTATES.

$5\ WO_3 . V_2O_5 . 4\ (NH_4)_2O + 13$ aq.
$10\ WO_3 . V_2O_5 . 6\ H_2O + 16$ aq.
$18\ WO_3 . V_2O_5 . 6\ H_2O + 30$ aq.

ANTIMONIO-TUNGSTATES.

$12\ WO_3 . 4\ Sb_2O_5 . 6\ K_2O + 25$ aq.

ANTIMONIO-MOLYBDATES.

$7\ MoO_3 . 4\ Sb_2O_5 . 5\ (NH_4)_2O + 12$ aq.

PYROPHOSPHO-TUNGSTATES.

$22\ WO_3 . 9\ P_2O_5 . 6\ Na_2O . 14\ (NH_4)_2O + 31$ aq.
$22\ WO_3 . 9\ P_2O_5 . 18\ K_2O + 49$ aq.
$22\ WO_3 . 9\ P_2O_5 . 13\ K_2O + 49$ aq.

MONOMETAPHOSPHO-TUNGSTATES.

† $16\ WO_3 . 2\ \{PO_3K\}\ 5\ Na_2O + 20$ aq.
$24\ WO_3 . 2\ \{PO_3K\}\ 3\ K_2O + 20$ aq.
$18\ WO_3 . 2\ \{PO_3NH_4\}\ (NH_4)_2O + 11$ aq.

MONOMETAPHOSPHO-MOLYBDATES.

$10\ MoO_3 . 4\ \{PO_3NH_4\} . 3\ (NH_4)_2O + 9$ aq.

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HEXAMETAPHOSPHO-MOLYBDATES.

† $14\ MoO_3 . \{Ba_3 . 6\ PO_3\} . BaO + 55$ aq.

ORTHOMETAPHOSPHO-TUNGSTATES.

$22\ WO_3 . 3\ \{P_2O_5 . 3\ K_2O\}\ \{6\ PO_3Na\} . 2\ K_2O . 2\ Na_2O + 42$ aq.

PHOSPHO-VANADIO-MOLYBDATES.

$48\ MoO_3 . 2\ P_2O_5 . V_2O_5 . 7\ (NH_4)_2O + 30$ aq.
$14\ MoO_3 . P_2O_5 . 8\ V_2O_5 . 8\ (NH_4)_2O + 50$ aq.

PHOSPHO-VANADIO-TUNGSTATES.

$60\ WO_3 . 3\ P_2O_5 . V_2O_5 . 10\ (NH_4)_2O + 60$ aq.
$16\ WO_3 . P_2O_5 . 3\ V_2O_5 . 5\ (NH_4)_2O + 37$ aq.
$60\ WO_3 . 3\ P_2O_5 . 2\ V_2O_5 . 18\ BaO + 144$ aq.
$18\ WO_3 . 3\ P_2O_5 . 4\ V_2O_5 . 8\ K_2O + 32$ aq.
† $7\ WO_3 . P_2O_5 . V_2O_5 . 3\ K_2O + 11$ aq.

VANADICO-VANADIO-MOLYBDATES.

$28\ MoO_3 . VO_2 . 4\ V_2O_5 . 11\ (NH_4)_2O + 20$ aq.
$30\ MoO_3 . 3\ VO_2 . 2\ V_2O_5 . 14\ BaO + 48$ aq.

VANADICO-VANADIO-TUNGSTATES.

$12\ WO_3 . 3\ VO_2 . 2\ V_2O_5 . 6\ Na_2O + 43$ aq.
$12\ WO_3 . 3\ VO_2 . 2\ V_2O_5 . 6\ (NH_4)_2O + 12$ aq.
$12\ WO_3 . 3\ VO_2 . 2\ V_2O_5 . 6\ Ag_2O + 8$ aq.

STANNO-PHOSPHO-MOLYBDATES.

$16\ MoO_3 . 4\ SnO_2 . 3\ P_2O_5 . 3\ (NH_4)_2O + 28$ aq.

STANNO-PHOSPHO-TUNGSTATES.

$22\ WO_3 . 2\ SnO_2 . P_2O_5 . 2\ (NH_4)_2O + 15$ aq.

PHOSPHO-VANADIO-VANADICO-TUNGSTATES.

$60\ WO_2 . 3\ P_2O_5 . V_2O_5 . VO_2 . 18\ BaO + 15$ aq.

To these I will add the new formulas of the salts described by Struve and Parmentier: —

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STRUVE'S SALTS.

$Al_2O_3 . 12\ MoO_3 . 6\ K_2O + 20$ aq.
$Al_2O_3 . 12\ MoO_3 . 6\ (NH_4)_2O + 20$ aq.
$Al_2O_3 . 12\ MoO_3 . 6\ Na_2O + 22$ aq.*
$Fe_2O_3 . 12\ MoO_3 . 6\ K_2O + 20$ aq.
$Fe_2O_3 . 12\ MoO_3 . 6\ (NH_4)_2O + 20$ aq.
$Cr_2O_3 . 12\ MoO_3 . 6\ K_2O + 20$ aq.
$Cr_2O_3 . 12\ MoO_3 . 6\ (NH_4)_2O + 20$ aq.
$Cr_2O_3 . 12\ MoO_3 . 6\ Na_2O + 21$ aq.
$Mn_2O_3 . 16\ MoO_3 . 5\ K_2O + 12$ aq.
$Mn_2O_3 . 16\ MoO_3 . 5\ (NH_4)_2O + 12$ aq.

PARMENTIER'S SALTS.

$Al_2O_3 . 10\ MoO_3 . 2\ K_2O + 15$ aq.
$Fe_2O_3 . 10\ MoO_3 . 2\ K_2O + 15$ aq.?
$Cr_2O_3 . 10\ MoO_3 . 2\ K_2O + 15$ aq.?

* Gentele, Journal für prakt. Chemie, lxxxi. 413.

CAMBRIDGE, July 8, 1885.

(To be continued.)

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IV.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF HARVARD COLLEGE.

XXV. — ATMOSPHERIC ELECTRICITY AT HIGH ALTITUDES.

By Alexander McAdie, M.A.

Communicated June, 1885.

The following experiments were made at Blue Hill Observatory during the month of June, 1885. The summit of the Hill has an elevation of 635 feet above sea level, and is therefore the highest point on this section of the Atlantic seaboard. With the exception of the two or three other hills in the range, all the surrounding country is very low and level. The average elevation is below 100 feet. On all sides this low land is well watered, having rivers of fair size and many ponds. For these reasons it was thought profitable to make some observations on the electrical state of the atmosphere, similar in nature to a series made for the United States Signal Service at the Jefferson Physical Laboratory in Cambridge.

The following apparatus was taken to the summit, and employed as hereafter described: —

A Multiple Quadrant Electrometer, designed by Professor Trowbridge, a description of which may be found in the Proceedings of the American Academy, June, 1885.

A portable battery of 100 Beetz cells, set up in series.

A second battery of the same kind, the cells arranged for convenience in sets of ten.

A newly set up Daniell cell.

Two large light kites, silk-covered and tinfoiled on the front face; the longest axes of the kites being over 4 feet.

1,500 feet of strong hemp fish-line, around which in a close spiral was wound No. 22 uncovered copper wire.

50 feet of insulated office wire, and some 10 or 12 feet of rubber tubing, to better insulate the office wire.

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One electrometer commutator, and some binding screws.

A condenser, with a capacity of $\frac{1}{3}$ farad, was also brought up, but when required for use was found to be defective and of no value.

The first observations were made on June 17, at nine A. M.

The first step was to measure the difference between the potential of the air, at a point a few feet out from the observatory walls and about five feet above the ground, and the ground potential. Instead of using the insulated water-dropper devised by Sir William Thomson, I made use of the method employed with success at Cambridge; namely, of dropping water on an insulated metallic plate, and allowing it to fall in drops therefrom. Making the electrometer connections in the way adopted by Thomson and English writers generally, — that is, connecting one set of quadrants with the insulated plate, the other set with the ground, and bringing the needle to a high potential by connecting with the plus pole of a battery of high electromotive force, — the electrometer indicated no appreciable difference between the potential of the air at that point and the potential of the ground. The ground, it may be remarked, was not at the observatory itself, — for the summit is a ledge of solid rock, — but a telephone ground, made of a wire running down the hillside some distance, and connected at different places with metallic plates buried in the earth.

Using the method adopted by Mascart in making the electrometer connections, — that is, connecting one set of quadrants to the plus pole of the 100-cell battery, and the other set of quadrants to the negative pole of the same battery, while the needle is connected with the insulated plate or body whose potential is to be determined, — no appreciable deflection due to the difference between the potentials of the air and ground could be noticed. The insulated plate has to be disconnected, and in its stead the ground substituted in order to ascertain this difference of potential. The electrometer is designed to measure only where differences of potential exist that are of considerable value. The needle of the electrometer carries a fine aluminium pointer, allowing one to read the deflections directly.

In the mean while, the kite having been raised to an elevation of 200 feet, the wired kite-string was now connected with one set of quadrants, and the other set connected with the ground. The needle was connected with the plus pole of the 100-cell Beetz battery, the other pole being grounded. Great care was taken to insulate very thoroughly the kite-string, as with electricity of high tension ordinary methods of insulation are not sufficient. Instantly on making connection, the needle was deflected with a considerable impulse beyond the

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limit of the scale (25 scale divisions), and until stopped by the side of the case of the instrument. The deflection indicated a very high positive potential for the air in the vicinity of the kite. To decrease the sensibility of the instrument, the battery charging the needle was reduced from 100 cells to 10 cells, and finally to a single cell. The Beetz battery of 100 cells has a difference of potential between its plus and minus poles of about 100 volts. The needle-pointer being at 0, the plus pole of the battery being connected to one set of quadrants, caused a deflection of 5.5 scale divisions. Connecting the insulated kite-string to the same terminal, the aluminium pointer was deflected with force to the side of the case. The least value of the difference between the kite potential and the ground was about 500 volts. The wind at this time was blowing freshly from the northwest, and the kite was seemingly stationary. Touching the ground wire, for a second, to the kite wire, a small spark about one twentieth of an inch in length was obtained. This, of course, discharged the wire, and the pointer returned to 0, returning, however, almost at once, again to the side of the case. In the hope of getting the deflection within the limits of the scale of the instrument, the quadrants connected with the ground were instead connected with the plus pole of the 100-cell Beetz battery. The deflection under this arrangement would represent the excess value of the air potential over that of the battery terminal. The deflection, however, still remained off the scale, though evidently not very distant. This deflection was maintained all the forenoon. The sky was covered with a low pallium of dark stratus clouds, and the weather was generally muggy and threatening. At three P. M. the kite was sent up as before. The same character of deflection prevailed, and the sparks obtained on connecting the ground with the kite wire were larger and as frequent as in the morning. The shock felt on touching these two wires with the fingers slightly moistened was about the same as one gets from a small-sized Leyden jar. The weather had cleared up, and it was now a clear and pleasant June afternoon. The wind was less steady than in the morning, coming more in puffs. In consequence of this, the kite was less steady, and kept rising and falling. Every time, without exception, when the kite would rise, the needle indicated an increase in the potential; and, on the other hand, as regularly as the kite fell the deflection decreased. When the kite would get apparently within 100 feet of the ground, the deflection would often fall to 8, 10, and sometimes less, of the scale divisions. The movements of the kite were told from watching the movements

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of the needle, and about as quickly as they could be seen from without.

On June 18, at 2 h. 30 m., P. M., these experiments were repeated. As before, no difference could be detected between the potential of the air a few feet from the ground, and that of the ground. It is to be remembered, however, that in the present adjustment of the electrometer, a difference equivalent to two volts was the minimum difference that could be detected. With the same instrument, adjusted for greater sensitiveness, employing the same methods, I have found in another locality a difference equivalent to a volt and more between a point in air 10 feet from the ground and the ground itself. The sky had been perfectly cloudless for many hours, and was now without clouds, except one or two very small rounded cumuli in the east. These also in the course of an hour disappeared, and the sky was again cloudless. The height of the kite was determined experimentally, by sending up a carrier on the kite-string, to which was attached thread, with markers at certain distances, made of folded wrapping paper, and of just sufficient weight to keep the thread perpendicular. The distance between the last marker and a level line of sight from the summit was estimated, and added to the known length of thread. My own carrier device having failed, Mr. Willard Gerrish, of the Observatory, suggested a conical-shaped carrier, which answered well. When the kite was about 350 feet high, the needle was deflected off the scale, but did not press against the side of the case of the instrument. When the kite was about 200 feet high, the deflections were in the neighborhood of 10, and variable in character. At this time, then, it was easily possible to notice and record the fluctuations in the value of the potential of the air. At times the needle would start suddenly and swing off the scale; sometimes remaining off, sometimes immediately returning. At other times it would fall to 5, 7, or 8, and either remain at these figures for a while, or vary greatly therefrom.

At 4 h. 30 m., with a cloudless sky, the kite being at a height of 300 feet, the deflection was 23+. The kite was then pulled down until only about half as high as before, and the average deflection was 15+. At 4 h. 50 m., the kite being about 400 feet high, the length of kite-string being about 700 feet, and the distance between the kite and the ground beneath it about 1,000 feet, there being a deep glen between this and the next hill, the deflection was off the scale, and apparently much greater than when at 300 feet. The sparks obtained by presenting the ground-wire to the kite-wire were larger than before,

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being about one eighth of an inch in length. The sky was perfectly cloudless at this time. As the kite remained very steady, it was fastened, and allowed to remain up until near eleven o'clock. The deflection of the needle was observed at frequent intervals, and the needle then brought back to the zero by connecting with the ground.

At eight P. M. the kite was more to the northeast than before, but at about the same elevation. The deflections, however, were much less than during the rest of the day, and for the most part within the scale limits. The needle kept constantly moving, but with little of the vigor it had previously shown. The character of the deflections may be illustrated by the following record for a single minute: —

Time. June 19. 1885, P. M. h. m. s.	Deflection.	Character.	Equivalent in Volts to
8 4 0	24+	Steady.	Over 500
10	10	Variable.	" 200
20	8	Decreasing steadily.	" 150
30	15	Very variable.	" 300
40	15	Variable, increasing and decreasing.	" 300
50	8 to 15	Variable.	" 150
8 5 0	10		" 200

The movements of the kite at this time appeared to be very slight, and one would be apt to suppose too small to account for the great potential changes. But it must be noticed that the movements of the kite, as far as they could be made out, were always in the proper direction to correspond with the character of the potential changes; that is, a rise in the position of the kite was attended with an increasing potential, and a fall attended with a decreasing potential.

At 8 h. 20 m. the deflection was very steady in character, and about 18. The potential indicated by that deflection was not sufficient to give a spark. Fifteen minutes later fair-sized sparks could be obtained at very short intervals. At nine o'clock the same condition prevailed. At ten o'clock the sparks were larger and more frequent. The sky during the whole time was cloudless.

The morning of June 19 was cloudless but hazy, and there was not sufficient wind to fly the kite. In the late afternoon, the wind having freshened from the southwest, the kite was raised to an elevation of about 500 feet above the summit. The kite remaining steady, the deflection was beyond the range of the instrument, and evidently greater than had yet been obtained. Large sparks could be obtained every few seconds by presenting the ground-wire to the kite-wire.

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The observatory at Blue Hill is provided with a self-registering anemoscope and a self-registering anemometer. It was originally intended to get a record of the potential variations, and compare it with the records of these two instruments. Unfortunately, both had to be returned to the maker for alterations, because of changes made in the building. It also became apparent that some form of self-recording electrometer was needed. I believe that by means of self-recording instruments the subject of atmospheric electricity can be most advantageously studied. The main purpose in these experiments was to show that it is possible to get some knowledge of the electrical condition of the air at a distance from the ground, with the imperfect means now at our command.

The one point of striking interest in these experiments is the obtaining evidence of this high electrical potential in a sky free from clouds. It will perhaps afford an argument against the necessity of considering condensation in explaining the origin of atmospheric electricity.

It may still be questioned whether these experiments prove that the potential of the air is positive, and increases steadily with increase in elevation. The effects observed may possibly be due to the friction of the air against the tinfoiled kite. My own opinion inclines to the former belief. Questions of this nature, however, can be definitely settled by the results of many and long observations. To accomplish these it is indispensable that a self-recording electrometer be devised, so that the records obtained may be directly comparable with the continuous records of the more prominent meteorological conditions.

I am much indebted to Mr. A. Lawrence Rotch, of the Observatory at Blue Hill, for assistance in carrying on these experiments.

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V.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON SUBSTITUTED PYROMUCIC ACIDS.

FIRST PAPER.

By Henry B. Hill and Charles R. Sanger.

Communicated November 12, 1884.

ON BROMPYROMUCIC ACIDS.

Although pyromucic acid has long been known and has been made the subject of many investigations, its behavior toward the halogens has been studied by but few chemists. As early as 1837 Malaguti * showed that ethyl pyromucate, when treated with dry chlorine, took up four atoms of chlorine forming the ethyl ether of pyromucic tetrachloride. This ether he treated with potassic hydrate, but isolated no product resulting from this decomposition. In 1865 Schmelz and Beilstein † studied the action of aqueous chlorine and bromine upon the acid, and described the resulting four-carbon compounds mucochloric and mucobromic acids. A few years later Limpricht,‡ with several of his pupils, pursued the subject further in the same direction, and isolated, among the products formed by the action of bromine and water upon pyromucic acid, fumaric acid, and its half aldehyde; they made, however, no experiments concerning the action of dry bromine. Toennies,§ working in Baeyer's laboratory, in 1878, prepared the pyromucic tetrabromide by the action of dry bromine upon pyromucic acid, and found that it could be converted into a dibrompyromucic acid melting at 184–186° by the action of alcoholic potash. Toennies did not publish, however, any very extended description of this acid, although he mentions its stability in resisting the action of various oxidizing

* Ann. Chim. Phys., lxiv. 282; lxx. 371.

† Ann. Chem. u. Pharm., Suppl., iii. 276.

‡ Ann. Chem. u. Pharm., clxv. 253.

§ Berichte d. deutsch. chem. Gesellsch., xi. 1086; xii. 1203.

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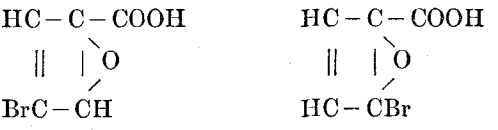
agents, and describes a derivative resulting from the action of bromine water, to which he gives the formula $C_4H_2Br_2O_2$. By heating the pyromucic tetrabromide he also obtained an acid melting at 180°, to which he assigned no formula, but which from his analyses was evidently a monobrompyromucic acid.

About the time of Toennies's first publication, Schiff and Tassinari * described two acids which they had obtained by allowing one molecule of bromine to act upon ethyl pyromucate, and decomposing the product thus obtained by alcoholic potash. These acids contained but one atom of bromine, one melted at 180° the other at 157°, and they were named by Schiff and Tassinari the α and β monobrompyromucic acids. The only statement which they make, beyond a mere description of the physical properties of the two acids, is that one acid may be converted into the other by continued boiling with concentrated hydrochloric acid. This change they consider analogous to the conversion of β-bromcinnamic acid into α-bromcinnamic acid under similar circumstances, and following this analogy they assign to the two acids the formulæ



In a paper published rather more than a year after the appearance of a preliminary note upon this subject by one of us,† Canzoneri and Oliveri,‡ without in any way alluding to this previous publication, described certain salts of the dibrompyromucic acid of Toennies and of one of the monobrompyromucic acids of Schiff and Tassinari, while they showed that the isomeric acid melting at 157° had no real existence. Our own experiments had already led us to the same conclusion.

Since of the various acids which could be formed by the replacement of the hydrogen atoms of pyromucic acid by halogens at most but three had been prepared, and none of these had been studied in any detail, we undertook the preparation and study of the brompyromucic acids. In the preparation of pyromucic tetrabromide, which first attracted our attention, we found it impossible to prevent completely the evolution of hydrobromic acid. Since Toennies's analysis of a product

* Berichte d. deutsch. chem. Gesellsch., xi. 842; Gazzetta Chimica, viii. 297.

† Berichte d. deutsch. chem. Gesellsch., xvi. 1130.

‡ Gazzetta Chimica, xiv. 173.

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formed by heating the tetrabromide had shown that a monobrompyromucic acid could thus be formed, we attempted to prepare it by heating the tetrabromide carefully in an oil bath. Although bromine was set free together with hydrobromic acid and monobrompyromucic acid was formed, we did not succeed in making the reaction available for the preparation of this acid on a larger scale. If, on the other hand, the bromine was allowed to act upon the pyromucic acid at the outset at higher temperature, there was little difficulty in securing abundant substitution and excellent product. At first we used glacial acetic acid as a solvent to facilitate the reaction, but we afterwards found that we could easily dispense with it, and that we could at our pleasure replace one or two hydrogen atoms in the pyromucic acid by bromine by varying the conditions of the reaction. The monobrompyromucic acid formed in this way melted at 183–184°, and appeared to be identical with that already described by Schiff and Tassinari, as far as could be judged from their meagre description, while the dibrompyromucic acid was new and melted at 167–168°.

In studying the action of alkalies upon the pyromucic tetrabromide, we found that the product formed was a mixture of two isomeric dibrompyromucic acids, one of which was identical with that formed by the direct action of bromine upon pyromucic acid, while the second melted at 190–191°, and was presumably identical with that which Toennies had prepared in the same way, although he had not obtained it in a state of perfect purity. While we have been wholly unable to verify the assertion of Schiff and Tassinari, that a monobrompyromucic acid exists, whose melting-point is 157°, we have found that a new monobrompyromucic acid melting at 128–129° can be made by the reduction of either of the two dibrompyromucic acids. We have also found it a matter of no difficulty to prepare tribrompyromucic acid, either by direct substitution from one of the dibrompyromucic acids, or by decomposing with alkalies the monobrompyromucic tetrabromide.

These various substituted pyromucic acids are in many respects more stable than pyromucic acid itself, and we have been able to determine the relative position of the several bromine atoms through a study of their oxidation products.

δ-Monobrompyromucic Acid.

Bromine acts upon pyromucic acid readily at 100° and forms a monobrompyromucic acid. To insure a satisfactory yield we have

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found it necessary to add the bromine slowly, and to take care that no liquid bromine comes in contact with the pyromucic acid. We have accomplished this very conveniently by hanging inside the flask containing the pyromucic acid a small glass cup, so arranged as to catch the liquid dropping from the reverse cooler and drop-funnel with which the flask is fitted. If the flow of the bromine be carefully regulated and the flask heated in a water bath, the process requires little attention. The reaction, however, is not perfectly smooth. Carbonic dioxide is evolved, and, as more or less bromine is unavoidably lost with the escaping hydrobromic acid, considerably more than one molecule of bromine must be added to insure the best result. For 20 grammes of pyromucic acid we have found it best to use 36 grammes of bromine instead of the 28.57 grammes required by theory. When the reaction is over, the product is dissolved in hot water, filtered, and the voluminous leafy crystals which separate on cooling are purified by recrystallization from hot water. If the bromine has not been added with due care the product may contain more or less dibrompyromucic acid, and is deposited then on cooling the hot aqueous solution in fine granular crystals. The dibrompyromucic acid may, however, readily be removed by precipitating an ammoniacal solution with baric chloride and acidifying the filtered solution with hydrochloric acid. We have not succeeded in obtaining perfectly uniform results in the preparation of the acid, and the yield of pure product has varied between 40 and 60 per cent of the theoretical amount. While we have been unable to prove that isomeric monobrompyromucic acids are formed in the reaction, the properties of the β-monobrompyromucic acid subsequently described are such that a small quantity of it, if formed, might easily escape detection.

The acid crystallized from hot water and dried over sulphuric acid gave on analysis the following results :—

I. 0.2291 grm. substance gave 0.2629 grm. CO_2 and 0.0322 grm. H_2O.
II. 0.2571 grm. substance gave 0.2959 grm. CO_2 and 0.0400 grm. H_2O.
III. 0.1944 grm. substance gave 0.1912 grm. AgBr.
IV. 0.1993 grm. substance gave 0.1957 grm. AgBr.
V. 0.2085 grm. substance gave 0.2051 grm. AgBr.

	Calculated for $C_5H_3BrO_3$.	Found.				
		I.	II.	III.	IV.	V.
C	31.42	31.30	31.38			
H	1.57	1.56	1.73			
Br	41.89			41.85	41.78	41.86

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The δ-monobrompyromucic acid crystallizes from water in irregular leafy plates with pearly lustre which melt at 183–184°. It is readily soluble in alcohol or ether, sparingly soluble in cold chloroform or benzol, more freely soluble on heating. In carbonic disulphide or ligroin it is almost insoluble. In cold water it is sparingly soluble, but dissolves freely on heating. The solubility of the acid in water at ordinary temperatures we determined according to the method of V. Meyer. The acid solution was neutralized with baric carbonate and the barium dissolved precipitated with sulphuric acid.

I. 37.5965 grm. of a solution saturated at 16.5° gave 0.0500 grm. $BaSO_4$.
II. 36.6804 grm. of a solution saturated at 16.5° gave 0.0488 grm. $BaSO_4$.

The aqueous solution of the acid saturated at 16.5° therefore contained the percentages: —

I.	II.
0.22	0.22

Baric δ-Monobrompyromucate, $Ba(C_5H_2BrO_3)_2 . 4\,H_2O$. — By neutralizing an aqueous solution of the acid with baric carbonate we obtained the barium salt in the form of irregular pearly plates which were readily soluble in hot water, more sparingly in cold. The air-dried salt contained four molecules of water,* most of which it lost over sulphuric acid.

I. 1.2927 grm. of the salt lost at 105° 0.1563 grm. H_2O.
II. 1.3857 grm. of the salt lost at 105° 0.1676 grm. H_2O.

	Calculated for $Ba(C_5H_2BrO_3)_2 . 4\,H_2O$.	Found. I.	Found. II.
H_2O	12.23	12.09	12.10

I. 0.3394 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1527 grm. $BaSO_4$.
II. 0.4088 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1848 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_2BrO_3)_2$.	Found. I.	Found. II.
Ba	26.50	26.44	26.57

* Canzoneri and Oliveri assign to this salt the formula $Ba(C_5H_2BrO_3)_2 . 2\frac{1}{2}H_2O$. Since their analytical data agree with ours, their incorrect formula is evidently due to an error in calculation.

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The solubility of the salt in water at ordinary temperatures we also determined.

I. 8.1035 grm. of a solution saturated at 18° gave on precipitation with H_2SO_4 0.1226 grm. $BaSO_4$.

II. 7.3943 grm. of a solution saturated at 18° gave on precipitation with H_2SO_4 0.1122 grm. $BaSO_4$.

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt: —

I.	II.
3.36	3.37

Calcic δ-Monobrompyromucate, $Ca(C_5H_2BrO_3)_2 . 3\,H_2O$. — The calcium salt prepared by neutralizing an aqueous solution with calcic carbonate formed small prisms clustered in globular aggregations which were sparingly soluble in cold water, somewhat more readily in hot.

I. 1.4814 grm. of the air-dried salt lost at 100° 0.1682 grm. H_2O.

II. 3.1181 grm. of the air-dried salt lost at 100° 0.3534 grm. H_2O.

III. 0.2135 grm. of the air-dried salt gave on ignition with H_2SO_4 0.0614 grm. $CaSO_4$.

	Calculated for $Ca(C_5H_2BrO_3)_2 . 3\,H_2O$.	Found. I.	II.	III.
H_2O	11.40	11.35	11.33	
Ca	8.44			8.47

I. 0.3175 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1032 grm. $CaSO_4$.

II. 0.3939 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1281 grm. $CaSO_4$.

	Calculated for $Ca(C_5H_2BrO_3)_2$.	Found. I.	II.
Ca	9.53	9.56	9.57

The solubility of the calcium salt in water we determined by precipitating with ammonic oxalate the solution prepared according to the method of V. Meyer, and converting the calcic oxalate thus obtained into sulphate by ignition with sulphuric acid.

I. 17.9259 grm. of a solution saturated at 20° gave 0.0620 grm. $CaSO_4$.

II. 15.5795 grm. of a solution saturated at 20° gave 0.0528 grm. $CaSO_4$.

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The solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

I.	II.
1.07	1.05

Argentic δ-Monobrompyromucate, $AgC_5H_2BrO_3$. — The silver salt falls as a crystalline precipitate on the addition of argentic nitrate to an aqueous solution of the free acid. We prepared it, however, by precipitating a solution of the potassium salt with argentic nitrate, and recrystallized the product from boiling water. It formed small clustered plates sparingly soluble even in boiling water, which could be recrystallized without decomposition from hot water.

0.2321 grm. of the salt dried over sulphuric acid gave on precipitation with HBr 0.1465 grm. AgBr.

	Calculated for $AgC_5H_2BrO_3$.	Found.
Ag	36.24	36.25

Sodic δ-Monobrompyromucate, $NaC_5H_2BrO_3$. — On neutralizing the acid with sodic carbonate we obtained the sodium salt in the form of small radiated needles which proved to be anhydrous.

I. 0.4172 grm. of the salt gave on ignition with H_2SO_4 0.1388 grm. Na_2SO_4.

II. 0.6014 grm. of the salt gave on ignition with H_2SO_4 0.1993 grm. Na_2SO_4.

	Calculated for $NaC_5H_2BrO_3$.	Found. I.	Found. II.
Na	10.80	10.78	10.74

Potassic δ-Monobrompyromucate, $KC_5H_2BrO_3$. — The potassium salt crystallized in irregular flattened prisms which were very soluble in water, and contained no water of crystallization.

I. 0.3118 grm. of the salt gave on ignition with H_2SO_4 0.1191 grm. K_2SO_4.

II. 0.3384 grm. of the salt gave on ignition with H_2SO_4 0.1285 grm. K_2SO_4.

	Calculated for $KC_5H_2BrO_3$.	Found. I.	Found. II.
K	17.07	17.15	17.05

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Ethyl δ-Monobrompyromucate, $(C_2H_5)C_5H_2BrO_3$. — The ethyl ether of the acid can readily be made by heating the acid with absolute alcohol and concentrated sulphuric acid, or by the action of ethyl iodide upon the silver salt * It may conveniently be prepared by warming for several hours on the water bath a mixture of four parts of absolute alcohol and three parts of concentrated sulphuric acid with four parts of the acid. A portion of the ether separates while the mixture is still hot, and on cooling and precipitating with water the quantity of ether obtained is nearly equal to that of the acid taken. The ether, washed with a dilute solution of sodic carbonate, and dried with calcic chloride, had a fragrant odor resembling ethyl pyromucate, and boiled between 234.5° and 236.5°, the greater portion showing a constant boiling-point of 235° † (mercury column completely in vapor) under a pressure of 767 mm. Since it retained a slight

* We attempted at first to prepare this ether by saturating the alcoholic solution of the acid with hydrochloric acid gas. The product which we thus obtained boiled at 132° under a pressure of 20 mm., and showed no signs of crystallization when strongly cooled. An analysis showed that this product contained much too high a percentage of halogen, and the results agreed quite closely with those required by the formula $(C_2H_5)C_5H_4BrCl_2O_3$.

	Calculated for $(C_2H_5)C_5H_4BrCl_2O_3$.	Found.	
$BrCl_2$	51.71	51.84	52.28

This behavior of the acid requires further investigation.

† The thermometer used was a "Zincke" thermometer made by Geissler. It gave the boiling-point of pure naphthaline under a pressure of 769 mm. with the mercury column completely in vapor as 217.6°. According to Crafts (Am. Journal Chemistry, v. 324) this boiling-point is about one degree too low, although it agrees exactly with that taken by Geissler in the graduation of his thermometers. Several years ago I gave the boiling-point of a specimen of ethyl pyromucate prepared by Mr. J. J. Thomsen as 195° under a pressure of 766 mm. (these Proceedings, vol. xvi. (N. S. viii.) p. 160), this boiling-point being materially lower than that given by Malaguti (Ann. Chim. Phys., [2,] lxiv. 279), 208–210°, under a pressure of 756 mm. Since Canzoneri and Oliveri have recently given the boiling-point of the ether as 205–208°, I have thought it worth while to repeat the determination. The thermometer I had previously used was made by Geissler, but I had neglected to determine its correctness above 200° by means of the boiling-point of naphthaline. An entirely different preparation of the ether, which melted at 34–35° (somewhat higher than the old preparation), showed with the above 'Zincke" thermometer the constant boiling-point 195° under a pressure of 769 mm., the mercury column being completely in the vapor. The ether was then allowed to stand for eighteen hours with fused calcic chloride, the temperature being for a great part of the time just above the melting-point of the ether. The boiling-point was still found to be constant at 195° under a pressure of 768 mm.

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yellowish tinge after several distillations, we distilled it for analysis under diminished pressure, and found it to boil at 133–134° under a pressure of 31 mm. On cooling, the ether crystallized in clear prisms with bevelled ends. The melting-point of the solidified ether was found to be 17°, and when the liquid ether was cooled to 13°, and a crystal of the solid ether introduced, the thermometer rose to 17°. The specific gravity of the ether at 20° referred to water at the same temperature we found to be 1.528.

Analyses I. and II. were made with substance prepared from the silver salt; III. and IV. from substance made with sulphuric acid.

I. 0.2171 grm. substance gave 0.1875 grm. AgBr.
II. 0.1616 grm. substance gave 0.1380 grm. AgBr.
III. 0.3571 grm. substance gave 0.3042 grm. AgBr.
IV. 0.3080 grm. substance gave 0.2623 grm. AgBr.

	Calculated for $(C_2H_5)C_5H_2BrO_3$.	Found. I.	II.	III.	IV.
Br	36.52	36.76	36.35	36.25	36.23

δ-*Monobrompyromucamide*, $C_5H_2BrO_2NH_2$. — Concentrated aqueous ammonia acts but slowly upon the ether in the cold, and several days are necessary to complete the reaction. At 100° in a sealed tube the decomposition is perfect in a few hours, but the yield of the amide is apparently not so satisfactory. The product of the reaction when recrystallized from boiling water forms long shining needles which melt at 144–145°. They are sparingly soluble in cold water, readily in hot, readily soluble in alcohol, ether, chloroform, or in hot benzol, sparingly soluble in cold benzol or carbonic disulphide. For analysis the substance was recrystallized from boiling water and dried over sulphuric acid.

0.7761 grm. substance gave 50.6 c.c. of moist nitrogen at 20°, and under a pressure of 747 mm.

	Calculated for $C_5H_2BrO_2NH_2$.	Found.
N	7.37	7.46

δ-*Monobrompyromucic tetrabromide*. — When exposed to an atmosphere of bromine, the δ-monobrompyromucic acid takes up four atoms of bromine. The addition product is readily soluble in alcohol or ether, is decomposed by water, but may be recrystallized from glacial acetic acid. It forms fine needles which decompose without melting at 173°.

0.1948 grm. substance gave 0.3594 grm. AgBr.

	Calculated for $C_5H_3Br_5O_3$.	Found.
Br	78.29	78.52

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Action of Bromine and Water.

Since pyromucic acid itself is readily attacked by aqueous bromine, and converted, according to the conditions of the reaction, into fumaric aldehyd or mucobromic acid, it seemed to us of interest to study the behavior of the δ-monobrompyromucic acid under similar conditions. We have found that the products formed vary greatly according to the conditions chosen, but in every case they prove to contain but four carbon atoms.

The acid was suspended in about thirty times its weight of cold water, and the vapor of bromine slowly led in by means of a current of air. Two molecules of bromine were found necessary to complete the reaction. The strongly acid solution, when extracted repeatedly with ether, gave an acid sparingly soluble in cold water, more readily in hot, which, when recrystallized from hot water, proved to be free from bromine. The behavior of this acid on heating showed it to be fumaric acid. Its identity was further established by an analysis of the silver salt.

0.5462 grm. of the salt gave 0.6194 grm. AgBr.

	Calculated for $Ag_2C_4H_2O_4$.	Found.
Ag	65.46	65.13

Beside the fumaric acid could be isolated minute quantities of two acids which contained bromine, and which from their physical properties appeared to be dibromsuccinic and isodibromsuccinic acids. These acids were formed in much larger quantity when the bromine was rapidly added; considerably more than two molecules of bromine were required to complete the reaction, and at the same time a crystalline substance insoluble in water was then formed. The aqueous solution was filtered from this insoluble substance and extracted with ether. The ethereal extract upon evaporation left a white crystalline residue which contained but little fumaric acid, and proved to consist mainly of about equal quantities of two acids, which could be separated by repeated recrystallization from water. The more soluble acid could be obtained by slow evaporation in well-formed rhombic plates which melted at 165°, and which on analysis proved to contain the percentage of bromine required by isodibromsuccinic acid.

I. 0.2434 grm. of substance gave 0 3344 grm. AgBr.
II. 0.2427 grm. of substance gave 0.3305 grm. AgBr.

	Calculated for $C_4H_4Br_2O_4$.	Found.	
		I.	II.
Br	57.97	58.44	57.94

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The less soluble acid crystallized from hot water in well-defined prisms, which remained unchanged when heated to 200°. An analysis showed this acid to be ordinary dibromsuccinic acid.

0.2468 grm. substance gave 0.3363 grm. AgBr.

	Calculated for $C_4H_4Br_2O_4$.	Found.
Br	57.97	57.98

The aqueous solution from which the two dibromsuccinic acids had been extracted with ether still contained a certain amount of fumaric acid, which was obtained by evaporation and identified by qualitative tests.

The substance insoluble in water which had been formed by the action of bromine was recrystallized, first from alcohol, then from ligroin, and crystallized in colorless prisms which melted at 110–111°. Analysis showed the substance to be dibromfurfurantetrabromide.

I. 0.7407 grm. substance gave 0.2380 grm. CO_2 and 0.0284 grm. H_2O.

II. 0.2054 grm. substance gave 0.4259 grm. AgBr.

III. 0.1680 grm. substance gave 0.3476 grm. AgBr.

	Calculated for $C_4H_2Br_6O$.	Found. I.	II.	III.
C	8.79	8.76		
H	0.37	0.43		
Br	87.90		88.22	88.04

This substance will be more fully studied and the results presented to the Academy at a future time. The action of bromine upon the δ-monobrompyromucic acid under the conditions we have chosen may therefore be expressed by the following equations: —

$$C_5H_3BrO_3 + 2\ Br_2 + 3\ H_2O = C_4H_4O_4 + CO_2 + 5\ HBr.$$
$$C_5H_3BrO_3 + 3\ Br_2 + 3\ H_2O = C_4H_4Br_2O_4 + CO_2 + 5\ HBr.$$
$$C_5H_3BrO_3 + 3\ Br_2 = C_4H_2Br_6O + CO_2 + HBr.$$

Action of Nitric Acid.

On warming δ-monobrompyromucic acid with dilute nitric acid it is readily oxidized, carbonic dioxide is given off in abundance, and a small quantity of a yellowish oil distils over, which has not yet been further examined. For the complete oxidation of the acid we have found it best to take an equal weight of nitric acid (sp. gr. 1.42), diluted with four times its weight of water. The solution on cooling deposits crys-

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tals of fumaric acid, and still more may be obtained by evaporation. The weight of fumaric acid thus obtained amounted to a little more than sixty per cent of that calculated from the equation,

$$C_5H_3BrO_3 + 2\ O + H_2O = C_4H_4O_4 + CO_2 + HBr.$$

The acid recrystallized from water and dried at 100° gave on analysis the following results : —

0.1728 grm. substance gave 0.2613 grm. CO_2 and 0.0575 grm. H_2O.

	Calculated for $C_4H_4O_4$.	Found.
C	41.37	41.24
H	3.45	3.70

Beside the fumaric acid could be isolated a small quantity of an acid readily soluble in cold water, whose melting-point suggested the possibility of its being maleic acid. Since at the high temperature which we had employed in oxidation it was to be expected that the maleic acid formed would be almost entirely converted into fumaric acid, we repeated the oxidation with stronger nitric acid (sp. gr. 1.42) and kept the temperature carefully between 30° and 35°. At this temperature the oxidation went on vigorously, and constant cooling was necessary. For complete oxidation three parts of strong nitric acid were found to be advantageous. After the oxidation was complete, the gaseous products of the reaction were removed by a current of air, the solution was then diluted, filtered from a slight flocculent precipitate thus formed, and neutralized with baric hydrate. In this way was precipitated a sparingly soluble crystalline barium salt, which, when recrystallized from hot water and dried by exposure to the air, proved to have the percentage composition of baric maleate.

I. 1.0940 grm. of the air-dried salt lost at 158° 0.0794 grm. H_2O.
II. 0.7644 grm. of the air-dried salt lost at 160° 0.0551 grm. H_2O.

	Calculated for $BaC_4H_2O_4 . H_2O$.	Found. I.	Found. II.
H_2O	6.69	7.26	7.21

I. 0.5036 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.4675 grm. $BaSO_4$.
II. 0.2776 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.2579 grm. $BaSO_4$.

	Calculated for $BaC_4H_2O_4$.	Found. I.	Found. II.
Ba	54.58	54.58	54.62

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From the barium salt we made the acid by exact precipitation with sulphuric acid, and recrystallized it first from ether and afterwards from water. The acid thus prepared melted at 131–132°,* was very soluble in cold water, and by heating with hydrochloric acid in aqueous solution was converted into an acid having all the physical properties of fumaric acid. By the method just described we obtained about fifty per cent of the weight of baric maleate theoretically required; and since the method of separation was necessarily imperfect, we have not hesitated to assume that in the oxidation of δ-monobrompyromucic acid with nitric acid maleic acid is the product first formed, and that the fumaric acid obtained in the oxidation at higher temperature results only from the further alteration of this. While we have been unable to prove as yet the formation of maleic acid in the oxidation with bromine, even under the most favorable conditions, it seems to us that there can be little doubt that the reaction in this case is also essentially the same. The occurrence of isodibromsuccinic acid among the products of the action of bromine, while it does not prove this view to be correct, certainly is in its favor.

β-Monobrompyromucic Acid.

From either of the dibrompyromucic acids subsequently described may be obtained by careful reduction a new monobrompyromucic acid isomeric with that already described. Since the dibrompyromucic acid melting at 167–168° is more conveniently prepared in large quantity, we have used this in order to obtain material for investigation. We have obtained the best results by dissolving two parts of the acid in four parts of concentrated ammonic hydrate diluted with fourteen parts of water, and adding one part of zinc dust. The reduction begins at once, the solution becomes hot, and in a few minutes the reaction is completed. When the ammoniacal solution no longer gives with calcic chloride an immediate precipitate of the sparingly soluble calcium salt of the dibrompyromucic acid, it is filtered and acidified with hydrochloric acid. If the reduction has not been carried too far, the solution soon solidifies with fine felted needles of the β-monobrompyromucic acid. For the purification of the acid we have found it best to convert it into the calcium salt, and to reject that portion of the

* The melting-point of maleic acid is usually given as 130°, but Kékulé has recently given the higher melting-point 132°. — Ann. Chem. u. Pharm., ccxxiii. 186.

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salt which first separates from a dilute solution. The acid obtained by acidifying the concentrated solution we have then recrystallized from hot water. The acid dried over sulphuric acid gave on analysis the following results. The material used in Analysis IV. was made from the dibrompyromucic acid melting at 191–192°.

I. 0.5336 grm. substance gave 0.6117 grm. CO_2 and 0.0828 grm. H_2O.
II. 0.1996 grm. substance gave 0.1967 grm. AgBr.
III. 0.2064 grm. substance gave 0.2031 grm. AgBr.
IV. 0.2115 grm. substance gave 0.2089 grm. AgBr.

	Calculated for $C_5H_3BrO_3$.	Found. I.	II.	III.	IV.
C	31.42	31.26			
H	1.57	1.72			
Br	41.89		41.97	41.88	42.05

β-Monobrompyromucic acid is readily soluble in alcohol or ether, quite soluble in chloroform or benzol, more sparingly soluble in ligroin or carbonic disulphide. It is very readily soluble in hot water, and as the solution cools it separates at high temperatures as an oil; at lower temperatures, in fine silky needles, which melt at 128–129°. On heating, it sublimes readily without decomposition. The solubility of the acid in water at ordinary temperatures we determined by neutralizing the solution with baric carbonate and precipitating with sulphuric acid the barium dissolved.

I. 21.1125 grm. of a solution saturated at 20° gave 0.1598 grm. $BaSO_4$.
II. 15.7586 grm. of a solution saturated at 20° gave 0.1198 grm. $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the acid: —

I.	II.
1.24	1.25

Baric β-Monobrompyromucate, $Ba(C_5H_2BrO_3)_2H_2O$. — By neutralizing an aqueous solution of the acid with baric carbonate, and concentrating the solution on the water bath, we obtained the barium salt in the form of irregular leafy scales, which were sparingly soluble in cold water, readily in hot. The air-dried salt lost nothing over sulphuric acid, and proved to contain one molecule of water.

I. 0.9389 grm. of air-dried salt lost at 120° 0.0334 grm. H_2O.
II. 1.9210 grm. air-dried salt lost at 130° 0.0676 grm. H_2O.

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	Calculated for $Ba(C_5H_2BrO_3)_2H_2O$.	Found. I.	II.
H_2O	3.36	3.56	3.52

I. 0.8920 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.4005 grm. $BaSO_4$.

II. 0.6245 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.2816 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_2BrO_3)_2$.	Found. I.	II.
Ba	26.50	26.39	26.51

The solubility of the salt in cold water we determined according to the method of V. Meyer.

I. 6.1243 grm. of a solution saturated at 20° gave on precipitation with H_2SO_4 0.0581 grm. $BaSO_4$.

II. 3.3922 grm. of a solution saturated at 20° gave on precipitation with H_2SO_4 0.0317 grm. $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

I.	II.
2.11	2.07

Calcic β-Monobrompyromucate, $Ca(C_5H_2BrO_3)_2 . 3\ H_2O$.—The calcium salt we prepared by neutralizing an aqueous solution of the acid with calcic carbonate. It crystallizes in small clustered branching needles, which are sparingly soluble in cold water, more readily in hot. The salt is permanent in the air, but effloresces over sulphuric acid.

I. 1.1627 grm. of the air-dried salt lost at 120° 0.1314 grm. H_2O.

II. 1.8043 grm. of the air-dried salt lost at 120° 0.2047 grm. H_2O.

	Calculated for $Ca(C_5H_2BrO_3)_2 . 3\ H_2O$.	Found. I.	II.
H_2O	11.40	11.30	11.34

I. 0.4784 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1534 grm. $CaSO_4$.

II. 0.5696 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1838 grm. $CaSO_4$.

	Calculated for $Ca(C_5H_2BrO_3)_2$.	Found. I.	II.
Ca	9.53	9.43	9.49

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The solubility of the salt in cold water we determined by precipitating the saturated solution with ammonic oxalate, and converting the calcic oxalate thus obtained into calcic sulphate by ignition with sulphuric acid.

I. 11.3923 grm. of a solution saturated at 20° gave 0.0642 grm. $CaSO_4$.

II. 11.2016 grm. of a solution saturated at 20° gave 0.0625 grm. $CaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

I.	II.
1.74	1.72

Argentic β-Monobrompyromucate, $AgC_5H_2BrO_3$. — The silver salt is precipitated by the addition of argentic nitrate to an aqueous solution of the acid. For analysis, we prepared it from the sodium salt by precipitation, and purified it by recrystallization from hot water.

0.2503 grm. of the salt gave on precipitation with HBr 0.1586 grm. AgBr.

	Calculated for $AgC_5H_2BrO_3$.	Found.
Ag	36.24	36.41

Sodic β-Monobrompyromucate, $NaC_5H_2BrO_3$. — The sodium salt prepared by neutralizing an aqueous solution of the acid with sodic carbonate crystallized in globular masses and proved to be anhydrous.

I. 0.4338 grm. of the salt gave on ignition with H_2SO_4 0.1470 grm. Na_2SO_4.

II. 0.5577 grm. of the salt gave on ignition with H_2SO_4 0.1849 grm. Na_2SO_4.

	Calculated for $NaC_5H_2BrO_3$.	Found.	
		I.	II.
Na	10.80	10.98	10.74

Potassic β-Monobrompyromucate, $KC_5H_2BrO_3$. — On neutralizing the acid in aqueous solution with potassic carbonate we obtained the potassium salt in the form of flat rectangular plates which proved to be anhydrous.

I. 0.3443 grm. of the salt gave on ignition with H_2SO_4 0.1293 grm. K_2SO_4.

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II. 0.4727 grm. of the salt gave on ignition with H_2SO_4 0.1775 grm. K_2SO_4.

	Calculated for $KC_5H_2BrO_3$.	Found. I.	II.
K	17.07	16.86	16.86

Ethyl β-Monobrompyromucate, $(C_2H_5)C_5H_2BrO_3$. — The ethyl ether we have made by the action of ethyl iodide upon the silver salt, and also by heating a solution of the acid in absolute alcohol with concentrated sulphuric acid. It may conveniently be prepared by warming for several hours five parts of the acid with a mixture of five parts of absolute alcohol and three parts of concentrated sulphuric acid. A portion of the ether separates while the mixture is still hot, the rest may be precipitated after cooling by the addition of water. The product, well washed with water and a dilute solution of sodic carbonate, solidifies at low temperatures, and may be purified by repeated melting and pressing with filter-paper the crystals obtained by cooling. The ether crystallizes in transparent clustered prisms, and has a fragrant odor not unlike that of ethyl pyromucate. We found that it distilled without decomposition at 235–236° (mercury column completely in vapor) under a pressure of 768 mm., and that the greater portion boiled steadily at 235°. The thermometer in the solidifying distillate stood at 28°, while the melting-point, determined in the ordinary way in a capillary tube, we found to be 28–29°. The ether prepared from the silver salt by the action of ethyl iodide had the same melting-point, and was used in Analysis II.

I. 0.2194 grm. substance gave 0.1888 grm. AgBr.
II. 0.2120 grm. substance gave 0.1820 grm. AgBr.

	Calculated for $(C_2H_5)C_5H_2BrO_3$.	Found. I.	II.
Br	36.52	36.64	36.55

β-Monobrompyromucamide, $C_5H_2BrO_2NH_2$. — From the ethyl ether of β-monobrompyromucic acid can readily be made the corresponding amide by the action of concentrated aqueous ammonia, since the reaction progresses quite rapidly even at ordinary temperatures. The resulting product, when repeatedly crystallized from boiling water, formed fine silky needles which melted at 155–156°. It was readily soluble in alcohol, quite readily soluble in ether or boiling chloroform, more sparingly soluble in benzol, and almost insoluble in carbonic

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disulphide or ligroin. It was readily soluble in hot water, but sparingly soluble in cold water.

0.6771 grm. substance gave 46.5 c.c. of moist nitrogen at 22.5° and under a pressure of 741 mm.

	Calculated for $C_5H_2BrO_2NH_2$.	Found.
N	7.37	7.74

β-monobrompyromucic acid appears to form no stable addition product with bromine. When exposed to the vapors of bromine for two days, we found that it had gained but 30 per cent of its weight, while a gain of 168 per cent was required for the formation of a tetrabromide. This slight gain in weight and the abundant evolution of hydrobromic acid pointed to the formation of a dibrompyromucic acid, for which a gain of 41 per cent was required. The product gave little evidence of decomposition when boiled with water, and was almost wholly soluble in a dilute solution of sodic carbonate. When recrystallized once from glacial acetic acid it melted at 165–166°, and possessed the characteristic properties of βδ-dibrompyromucic acid. Bromine at ordinary temperatures had therefore replaced one atom of hydrogen by bromine.

Action of Bromine and Water.

When β-monobrompyromucic acid is treated with bromine in aqueous solution it is rapidly oxidized, and products are formed which are apparently analogous to those formed from pyromucic acid under similar conditions. One or two molecules of bromine were readily taken up in the cold. In either case, the clear aqueous solution, when extracted with ether, yielded viscous oily products which showed no signs of crystallization after standing for days in vacuo over sulphuric acid. The extremely uninviting character of these substances made us unwilling to spend more time upon them at present, more especially since we found that mucobromic acid was formed when three molecules of bromine were employed. The reaction in this case required heat for its completion, and from the concentrated solution mucobromic acid (melting-point 120–121°) crystallized on cooling. Since it is probable that the aldehyde acid with one bromine atom corresponding to mucobromic acid is formed by the action of two molecules of bromine, we hope in the future to study the reaction further.

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Action of Nitric Acid.

β-monobrompyromucic acid is readily oxidized by dilute nitric acid. In order to determine the product formed, we heated the acid with twice its weight of concentrated nitric acid (sp. gr. 1.42) diluted with five times its weight of water. After the oxidation was complete, we extracted the solution thoroughly with ether, and obtained, on evaporating the ether, a white crystalline acid which was readily soluble in water. After recrystallization from water it melted at 176–177°, and gave a percentage of bromine, which showed it to be monobromfumaric acid (isobrommaleic acid).

0.2300 grm. substance gave 0.2218 grm. AgBr.

	Calculated for $C_4H_3BrO_4$.	Found.
Br	41.03	41.04

By oxidation with nitric acid monobromfumaric acid had therefore been formed according to the equation,

$$C_5H_3BrO_3 + 3\ O = C_4H_3BrO_4 + CO_2.$$

ETHYL PYROMUCATE WITH ONE MOLECULE OF BROMINE.

We have made six fruitless attempts to prepare a monobrompyromucic acid melting at 156–157°, according to the method described by Schiff and Tassinari,* by the addition of one molecule of bromine to ethyl pyromucate, and the decomposition of the product thus obtained by an alcoholic solution of potassic hydrate. Aside from the δ-monobrompyromucic acid, which could readily be isolated, we have been able to find only the two isomeric dibrompyromucic acids hereafter described which result from the decomposition of the tetrabromide of the ethyl ether. In separating these two acids we followed the method which we had already found most efficacious, namely, the fractional crystallization of the calcium salts, but in other respects we adhered strictly to the directions given by Schiff and Tassinari. The acid obtained from the less soluble calcium salt melted at 166–167°, and crystallized from water in the twinned forms characteristic of the $\beta\delta$-dibrompyromucic acid.

0.1444 grm. substance gave 0.2020 grm. AgBr.

	Calculated for $C_5H_2Br_2O_3$.	Found.
Br	59.26	59.53

* Gazzetta Chimica, viii. 298.

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From the more soluble calcium salt we obtained the $\beta\gamma$-dibrompyromucic acid melting at 190–192°, which gave on analysis the proper percentage of bromine.

0.1955 grm. substance gave 0.2723 grm. AgBr.

	Calculated for $C_5H_2Br_2O_3$.	Found.
Br	59.26	59.29

Furthermore, it was not difficult to isolate in considerable quantity an acid containing but a trace of bromine, which melted at 129–130°, and which possessed in other respects the character of pyromucic acid. Our observations agree closely with those described by Canzoneri and Oliveri in the paper already mentioned,* with the single exception that they appear to have overlooked entirely the formation of the second dibrompyromucic acid melting at 167–168°. Since the two dibrompyromucic acids and unaltered pyromucic acid were formed from a product containing equal molecules of ethyl pyromucate and bromine, we were led to the conclusion that no dibromide had been formed under the conditions chosen, and that the supposed dibromide was in fact only a mixture of unaltered pyromucic ether with its tetrabromide. Since at ordinary temperatures quantities of hydrobromic acid were evolved on mixing the pyromucic ether with bromine,† (a fact not mentioned by Schiff and Tassinari or by Canzoneri and Oliveri,) it was evident that the monobrompyromucic acid which appeared among the products could readily have been formed by direct substitution. On submitting the mixture of equal molecules of pyromucic ether and bromine to fractional distillation in vacuo, it was easy to isolate among the more volatile products the ethyl ether of δ-monobrompyromucic acid and ethyl pyromucate, melting at 34–35°. The ethyl monobrompyromucate still contained ethyl pyromucate, since the percentage of bromine which we found was much too low.

0.1890 grm. substance gave 0.1487 grm. AgBr.

	Calculated for $(C_2H_5)C_5H_2BrO_3$.	Found.
Br	36.54	33.49

The acid obtained from the ether, when recrystallized from water, melted at 182–183°.

* Gazzetta Chimica, xiv. 173.

† The evolution of hydrobromic acid was invariably observed, although we varied in many ways the conditions under which the reaction took place. In addition to the glacial acetic acid recommended by Schiff and Tassinari as a solvent, we tried carbonic disulphide and chloroform with the same results.

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Action of Alcoholic Sodic Hydrate upon Pyromucic Tetrabromide.

By acting upon pyromucic tetrabromide with an alcoholic solution of potassic hydrate, Toennies obtained a dibrompyromucic acid melting at 186°. In the preliminary paper already referred to,* he gives no description of the conditions under which the decomposition was effected, and, as far as we are aware, he has never published any more extended account of his work.

The pyromucic tetrabromide we prepared according to his directions by exposing pyromucic acid to the vapors of bromine. The bromine was quite rapidly absorbed, and the acid was converted into a voluminous porous mass from which the excess of bromine could readily be expelled by a short exposure to the air. The formation of this addition product, however, was not the only reaction which took place, since hydrobromic acid was invariably evolved in no insignificant quantities, and the product therefore contained also δ-monobrompyromucic acid and its tetrabromide. For the purification of the pyromucic tetrabromide we have found glacial acetic acid (99.5 per cent) more advantageous than the mixture of ligroin and ether recommended by Toennies.

Since the purification of large quantities of the tetrabromide was at best a matter of difficulty, we have used in our work the crude product, more especially since the isolation of the products formed from it presented no greater difficulties. Instead of using an alcoholic solution of potassic hydrate for its decomposition, we have taken sodic hydrate, since the sodium salts of the acids formed seemed to be somewhat less soluble in alcohol than the potassium salts. We have found that the best results may be obtained by using a decided excess of a concentrated solution of the alkaline hydrate, taking care that the temperature does not rise above 25°. The greater part of the sodium salts formed separates at once, and may be filtered off upon the pump. The sodium salt dissolved in water and acidified with hydrochloric acid yields an acid, usually more or less colored, which is readily soluble in cold water, more readily in hot, and whose melting-point is quite constant (136–138°). This consists essentially of a mixture of two isomeric dibrompyromucic acids, although it frequently contains small quantities of δ-monobrompyromucic and tribrompyromucic acids. The aqueous solution filtered from these acids contains also oxalic acid.

* Berichte der deutschen chem. Gesellsch., xi. 1086.

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Although we have not found it possible to separate these acids directly by fractional crystallization, they may be separated by means of their calcium salts. While we have found it easy to prepare in this way small quantities of the pure acids, the complete separation of large quantities of the acids involves a very considerable amount of time and labor. We have found it most convenient to dissolve the mixed acids in ammonic hydrate, and to add calcic chloride to the dilute solution (1 : 30). A very sparingly soluble crystalline calcium salt is thus thrown down, which contains chiefly one of the two dibrompyromucic acids, while the calcium salts of the other acids remain in solution. The sparingly soluble calcium salt may be purified by recrystallization from boiling water, or the acid may be set free, the calcium salt reprecipitated, and the operation repeated until the melting-point of the acid is found to be 164–166°. The solution containing the more soluble calcium salts is acidified, and the acids thus obtained are separated by recrystallization from boiling water. The tribrompyromucic acid is almost insoluble in water, while the δ-monobrompyromucic acid, though but slightly more soluble in cold water than the dibrompyromucic acid, is present in such small quantity that its removal is a matter of little difficulty. When the melting-point of the dibrompyromucic acid has been raised to 184° by recrystallization from water, its further purification is effected by washing or recrystallizing from benzol. The acid whose calcium salt is more sparingly soluble in water, and which, as we shall afterward show, is the βδ-dibrompyromucic acid, melts at 167–168°, while the isomeric βγ-dibrompyromucic acid, whose calcium salt is more readily soluble, melts at 191–192°. Although we have made many attempts to control at will the quantities of the two dibrompyromucic acids formed, we have as yet met with no success. The yield of the mixed acids was far from satisfactory, and amounted to but from thirty-four to thirty-eight per cent of that theoretically required. The difficulties in the way of complete separation of the two acids make it impossible for us to give the precise ratio between the amounts of the two isomers found. While we have usually obtained nearly twice as much of the low-melting acid as of the high, we are inclined to think that the original mixture contained them in nearly equal quantities.

The alcoholic filtrate from the sodium salts contained, beside small quantities of these salts in solution, considerable quantities of sodic δ-monobrompyromucate. When diluted with water, it became turbid, with the separation of a small quantity of a colorless oil. In order to determine its nature, we distilled the filtrate with steam and precipi-

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tated the alcoholic distillate by the further addition of water. The oil which was thus thrown down was dried with calcic chloride and distilled under diminished pressure. The wide range in boiling-point (60–130° at 17 mm.) which we then observed showed its nature to be tolerably complex. After repeated distillations, we were able to isolate one fraction (A) boiling between 59° and 69° under 17 mm. pressure, and a somewhat larger fraction boiling at 94–99° under a pressure of 17 mm. This second fraction partially solidified on standing, and the crystals (B) were separated from the oily mother-liquor (C) by filtration. With a second larger quantity of the alcoholic filtrate subsequently obtained we adopted a somewhat different method. We precipitated the excess of sodic hydrate by carbonic dioxide, distilled the alcoholic filtrate, and precipitated the distillate with water. After several distillations in vacuo, we obtained one fraction (D) boiling at 57–62° under a pressure of 20 mm., a second (E) boiling at 61–68° under a pressure of 19 mm., and a third boiling at 98–102° under a pressure of 19 mm., which as before partially solidified on standing, and the crystals (F) were separated by filtration from the mother-liquor (G). The fractions boiling between 68° and 98° were insignificant in quantity.

The lower boiling fractions proved, on analysis, to contain a percentage of bromine, agreeing closely with that required by the formula $C_4H_2Br_2O$.

I. 0.2444 grm. of substance (A) gave 0.4060 grm. AgBr.
II. 0.2503 grm. of substance (A) gave 0.4160 grm. AgBr.
III. 0.3593 grm. of substance (D) gave 0.5959 grm. AgBr.
IV. 0.2559 grm. of substance (E) gave 0.4284 grm. AgBr.
V. 0.3416 grm. of substance (E) gave 0.5715 grm. AgBr.

	Calculated for $C_4H_2Br_2O$.	Found.				
		I.	II.	III.	IV.	V.
Br	70.79	70.69	70.74	70.58	71.25	71.19

The great variation in boiling-point with this slight variation in percentage composition renders it probable that the oil contained two isomeric dibromfurfurans. The fraction boiling at 61–68°, after standing for a few days, was unfortunately largely converted into an amorphous black solid; the lower fraction remained unaltered. When the lower fraction was treated with bromine, hydrobromic acid was evolved even at ordinary temperatures, so that no corresponding addition product could be prepared, and we have hitherto been unable to obtain

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by oxidation any products which would enable us to draw any conclusion as to its constitution.

The solid which separated from the higher fractions, on cooling when recrystallized from alcohol, formed broad flattened needles which melted at 77°. It was readily soluble in alcohol, ether, chloroform, or benzol, more sparingly soluble in carbonic disulphide or ligroin. The percentage of bromine which the substance contained agreed precisely with that required by the formula $C_4H_3BrO_2$. While the combustion of the substance gave a percentage of carbon materially greater than that which this formula requires, it seemed to us to leave no doubt of the composition of the substance. We were therefore unwilling to sacrifice the small amount of the substance which we had left in order to make a second combustion.

I. 0.5251 grm. of substance (F) gave 0.5742 grm. CO_2 and 0.0949 grm. H_2O.
II. 0.1523 grm. of substance (B) gave 0.1758 grm. AgBr.
III. 0.2186 grm. of substance (F) gave 0.2527 grm. AgBr.

	Calculated for $C_4H_3BrO_2$.	Found. I.	II.	III.
C	29.44	29.82		
H	1.84	2.01		
Br	49.09		49.14	49.19

The small amount of this substance at our disposal — we obtained but three grammes of the crude product from 2.6 kilogrammes of pyromucic tetrabromide — has made it impossible for us to submit it to any very extended investigation. In aqueous solution it reduces silver oxide, and at the same time argentic bromide is formed. We were unable, however, to isolate any definite products of the oxidation. With nitric acid, apparently nothing but oxalic acid was formed. It was unaffected by dry bromine, but when treated with bromine and water it was converted into an amorphous substance insoluble or sparingly soluble in all common solvents. It was readily decomposed by aqueous alkalies. The solution had a bright yellow color, and contained potassic bromide, but we have been unable to determine the products resulting from the reaction.

This ready decomposition in alkaline solution makes it probable that it was formed during the process of distillation, although it is perhaps possible that the small quantity which we were able to obtain was only that portion which chanced to escape decomposition in the

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original alkaline solution. It will be noticed that this substance is isomeric with a product obtained by Limpricht by the action of bromine upon pyromucic acid under conditions which he was unable to fix precisely. The higher melting-point, 84°, and the fact that it was unaffected by an alcoholic solution of potassic hydrate at 180°, establish with sufficient precision their essential difference.

The higher boiling fractions from which this crystalline substance had been separated as completely as possible gave, on analysis, a percentage of bromine, which showed that they consisted mainly of a tribromfurfuran. The difficulty of removing completely, by distillation or by freezing, the solid constituent, sufficiently explains the low percentages of bromine we have obtained.

I. 0.2312 grm. of substance (C) gave 0.4130 grm. AgBr.
II. 0.3253 grm. of substance (C) gave 0.5855 grm. AgBr.
III. 0.2897 grm. of substance (G) gave 0.5246 grm. AgBr.
IV. 0.2291 grm. of substance (G) gave 0.4130 grm. AgBr.

	Calculated for C_4HBr_3O.	Found.			
		I.	II.	III.	IV.
Br	78.68	76.03	76.61	77.05	76.74

This tribromfurfuran, when treated with bromine, gave off at ordinary temperatures clouds of hydrobromic acid, so that the corresponding addition product could not be prepared. We have also been unable as yet to obtain any definite oxidation products containing four carbon atoms.

The formation of dibromfurfuran from pyromucic tetrabromide evidently takes place according to the equation,

$$C_5H_4Br_4O_3 = C_4H_2Br_2O + CO_2 + 2\ HBr.$$

The tribromfurfuran must, of necessity, be formed from the monobrompyromucic tetrabromide which the crude pyromucic tetrabromide contains, —

$$C_5H_3Br_5O_3 = C_4HBr_3O + CO_2 + 2\ HBr.$$

$\beta\delta$-Dibrompyromucic Acid.

This acid is formed, as has already been explained, together with the isomeric $\beta\gamma$-dibrompyromucic acid, by the action of an alcoholic solution of sodic hydrate upon pyromucic tetrabromide. It may, how-

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ever, be more conveniently, if not more economically, prepared by the direct action of bromine upon pyromucic acid. The reaction is apparently quite complex, a large excess of bromine is required, and the product is small compared with that theoretically required. Pyromucic acid is treated with about three molecules of bromine, and heated on the water bath with reverse cooler, until the evolution of hydrobromic acid is over. There remains, then, in the flask a red viscous oil which contains $\beta\delta$-dibrompyromucyl bromide with a small amount of δ-monobrompyromucyl bromide, dibrommaleic acid or its anhydride, and other products not yet more exactly determined. This oil is washed with cold water to remove the more soluble products, and is then boiled with water until the acid bromides are converted into the acids. The separation of the dibrompyromucic from the monobrompyromucic acid with which it is mixed may be most conveniently effected by precipitating its barium salt from an ammoniacal solution by the addition of baric chloride, and repeating the operation until a product melting at 165-166° is obtained. By subsequent recrystallization from hot water and from benzol the melting-point may then be raised to 167–168°.

The acid thus purified gave, on analysis, the following results : —

I. 0.5370 grm. substance gave 0.4379 grm. CO_2 and 0.0390 grm. H_2O.
II. 0.2251 grm. substance gave 0.3125 grm. AgBr.
III. 0.1665 grm. substance gave 0.2323 grm. AgBr.

	Calculated for $C_5H_2Br_2O_3$.	Found. I.	II.	III.
C	22.22	22.24		
H	0.74	0.81		
Br	59.26		59.09	59.39

The $\beta\delta$-dibrompyromucic acid is readily soluble in alcohol or ether, freely soluble in boiling chloroform, quite readily soluble in benzol, but sparingly soluble in carbonic disulphide or ligroin. It is sparingly soluble in cold water, quite readily soluble in boiling water, and crystallizes on cooling in small oblique prisms, which, however, usually appear in characteristic twinned forms.

The solubility of the acid in water at ordinary temperatures we determined by neutralizing with baric carbonate the saturated solution, and determining by precipitation with sulphuric acid the amount of barium dissolved.

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I. 38.3346 grm. of a solution saturated at 20° gave 0.0462 grm. $BaSO_4$.

II. 38.3935 grm. of a solution saturated at 20° gave 0.0464 grm. $BaSO_4$.

According to these determinations the aqueous solution of the acid saturated at 20° contained the following percentages: —

I.	II.
0.28	0.28

Baric βδ-Dibrompyromucate, $Ba(C_5HBr_2O_3)_2 . 4 H_2O$. — The barium salt we prepared by neutralizing a boiling aqueous solution of the acid with baric carbonate. After recrystallization from boiling water, it formed fine branching needles. The air-dried salt contained four molecules of water, three of which it lost over sulphuric acid.

I. 1.4800 grm. of air-dried salt lost 0.1117 grm. H_2O over sulphuric acid, and in addition 0.0324 grm. H_2O at 110°.

II. 2.1113 grm. of the air-dried salt lost at 110° 0.2030 grm. H_2O.

	Calculated for $Ba(C_5HBr_2O_3)_2 . 4 H_2O$.	Found. I.	Found. II.
3 H_2O	7.23	7.54	
4 H_2O	9.64	9.74	9.60

I. 0.4109 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1415 grm. $BaSO_4$.

II. 0.7780 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.2666 grm. $BaSO_4$.

	Calculated for $Ba(C_5HBr_2O_3)_2$.	Found. I.	Found. II.
Ba	20.30	20.24	20.14

The solubility of the salt in cold water we determined by precipitating the saturated solution with sulphuric acid.

I. 38.7621 grm. of a solution saturated at 16° gave 0.0132 grm. $BaSO_4$.

II. 36.2526 grm. of a solution saturated at 16° gave 0.0129 grm. $BaSO_4$.

The aqueous solution saturated at 16° therefore contained the following percentages of the anhydrous salt: —

I.	II.
0.10	0.10

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Calcic βδ-Dibrompyromucate, $Ca(C_5HBr_2O_3)_2 . 3 H_2O$. — On neutralizing a boiling aqueous solution of the acid with calcic carbonate, we obtained the calcium salt in small clustered prisms, which we purified by recrystallization from boiling water. The air-dried salt contained three molecules of water, one of which it lost over sulphuric acid.

I. 1.1374 grm. of air-dried salt lost over sulphuric acid 0.0275 grm. H_2O, and in addition 0.0706 grm. H_2O at 110°.

II. 1.4733 grm. of the air-dried salt lost at 112° 0.0984 grm. H_2O.

	Calculated for $Ca(C_5HBr_2O_3)_2 . 3 H_2O$.	Found. I.	II.
H_2O	2.85	2.42	
$3 H_2O$	8.56	8.63	8.36

I. 0.4709 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1107 grm. $CaSO_4$.

II. 0.6026 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1387 grm. $CaSO_4$.

	Calculated for $Ca(C_5HBr_2O_3)_2$.	Found. I.	II.
Ca	6.92	6.91	6.77

The solubility of the salt in cold water we determined by evaporation and ignition with sulphuric acid.

I. 39.5194 grm. of a solution saturated at 17° gave 0.0288 grm. $CaSO_4$.

II. 50.3735 grm. of a solution saturated at 17° gave 0.0344 grm. $CaSO_4$.

The aqueous solution saturated at 17° therefore contained the following percentages of the anhydrous salt: —

I.	II.
0.31	0.29

Argentic βδ-Dibrompyromucate, $AgC_5HBr_2O_3$. — From an aqueous solution of the acid argentic nitrate precipitates the silver salt in the form of fine clustered needles, which may be recrystallized from hot water without essential decomposition. For analysis we prepared it by precipitating a solution of argentic nitrate with a solution of the acid neutralized by ammonic hydrate.

0.3275 grm. of the salt dried over sulphuric acid gave 0.1646 grm. AgBr.

	Calculated for $AgC_5HBr_2O_3$.	Found.
Ag	28.65	28.87

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Sodic βδ-Dibrompyromucate, $NaC_5HBr_2O_3 . 2 H_2O$. — The sodium salt we prepared by dissolving the acid in a solution of sodic carbonate, and subsequent recrystallization from water. It formed short needles, which were not very soluble in cold water, and which, when air-dried, contained two molecules of water.

I. 1.0207 grm. of the air-dried salt lost at 122° 0.1095 grm. H_2O.
II. 1.1177 grm. of the air-dried salt lost at 122° 0.1201 grm. H_2O.

	Calculated for $NaC_5HBr_2O_3 . 2 H_2O$.	Found. I.	Found. II.
H_2O	10.97	10.73	10.75

I. 0.5364 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1284 grm. Na_2SO_4.
II. 0.5492 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1314 grm. Na_2SO_4.

	Calculated for $NaC_5HBr_2O_3$.	Found. I.	Found. II.
Na	7.88	7.76	7.75

Potassic βδ-Dibrompyromucate, $KC_5HBr_2O_3$. — The potassium salt prepared by dissolving the acid in a dilute solution of potassic carbonate, and recrystallizing the product thus obtained from water, crystallized in long concentrically grouped needles, which proved to be anhydrous.

I. 0.5986 grm. of the salt gave on ignition with H_2SO_4 0.1691 grm. K_2SO_4.
II. 0.6018 grm. of the salt gave on ignition with H_2SO_4 0.1680 grm. K_2SO_4.

	Calculated for $KC_5HBr_2O_3$.	Found. I.	Found. II.
K	12.69	12.69	12.53

Ethyl βδ-Dibrompyromucate, $(C_2H_5)C_5HBr_2O_3$. — The ethyl ether we have made by the action of ethyl iodide upon the silver salt of the acid, and also by heating an alcoholic solution of the acid with concentrated sulphuric acid. By the latter method we have obtained a good yield by dissolving five parts of the acid in an equal weight of absolute alcohol, adding three parts of concentrated sulphuric acid, and warming for several hours at 100°. The product precipitated by the addition of water we washed with a dilute solution of sodic carbonate and purified by recrystallization from alcohol. It crystallized in small,

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flat, clustered prisms, which melted at 57–58°, and boiled with decided decomposition at 271–272° (mercury column completely in vapor), under a pressure of 765 mm. The ether has a pleasant, fragrant odor, not unlike that of ethyl pyromucate. It is readily soluble in ether, chloroform, benzol, or ligroin, somewhat less soluble in carbonic disulphide. It is readily soluble in hot alcohol, much more sparingly soluble in cold. The ether used in Analysis II. was made from the silver salt.

I. 0.1524 grm. substance gave 0.1927 grm. AgBr.
II. 0.2024 grm. substance gave 0.2556 grm. AgBr.

	Calculated for $(C_2H_5)C_5HBr_2O_3$.	Found. I.	II.
Br	53.69	53.83	53.74

βδ-Dibrompyromucyl Bromide, $C_5HBr_3O_2$. — It has already been said that βδ-dibrompyromucyl bromide is formed by the action of dry bromine upon pyromucic acid. In order to isolate it, we submitted the viscous oil which was thus formed to fractional distillation in vacuo. After repeated distillations a fraction was isolated, boiling at 149–155° under a pressure of 24 mm., most of which passed over between 153° and 155°. This fraction, on standing over sulphuric acid, gradually solidified, and the solid thus obtained could readily be purified by recrystallization from ligroin. On heating with water it formed βδ-dibrompyromucic acid; with alcohol, it gave the ether melting at 56–57°; and on analysis it gave the percentage of bromine required by the formula $C_5HBr_3O_2$. Analysis III. was made with material prepared from the crude product by crystallization alone without previous distillation.

I. 0.2214 grm. substance gave 0.3752 grm. AgBr.
II. 0.1876 grm. substance gave 0.3180 grm. AgBr.
III. 0.2152 grm. substance gave 0.3640 grm. AgBr.

	Calculated for $C_5HBr_3O_2$.	Found. I.	II.	III.
Br	72.07	72.11	72.14	71.99

The βδ-dibrompyromucyl bromide crystallizes in small compact prisms which melt at 45–46°. It is readily soluble in alcohol, ether, chloroform, or benzol, somewhat less soluble in ligroin. It is slowly attacked by cold water, more readily by hot.

From the lower fractions there separated, on standing, prismatic crystals, which, from their behavior and from their melting-point

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(114–115°), were shown to be dibrommaleic anhydride. In confirmation we prepared from the aqueous solution obtained by washing the crude product with cold water considerable quantities of baric dibrommaleate, which was identified by analysis.

0.5423 grm. of the air-dried salt gave on ignition with H_2SO_4 0.2853 grm. $BaSO_4$.

	Calculated for $BaC_4Br_2O_4 . 2 H_2O$.	Found.
Ba	30.78	30.93

Since the most volatile portions of the oil gave with water δ-monobrompyromucic acid, it contained doubtless the corresponding monobrompyromucyl bromide. The quantity, however, appeared to be so small that we made no attempt to isolate it.

βδ-Dibrompyromucamide, $C_5HBr_2O_2NH_2$. — Concentrated aqueous ammonia acts but slowly upon the ethyl ether of βδ-dibrompyromucic acid, and even after long standing the decomposition is imperfect. The amide may readily be made from the bromide just described by the action of aqueous ammonia, and may be purified by recrystallization from hot water. Thus prepared, it forms long silky needles which melt at 175–176°. It is readily soluble in alcohol, quite readily soluble in ether, chloroform, or hot benzol, and almost insoluble in carbonic disulphide or ligroin. It is sparingly soluble in cold water, but freely soluble in hot water.

0.9102 grm. substance gave 44.5 c.c. moist nitrogen at 14.5° and under a pressure of 722 mm.

	Calculated for $C_5HBr_2O_2NH_2$.	Found.
N	5.20	5.31

Action of Bromine and Water.

We found that the βδ-dibrompyromucic acid was rather slowly attacked by bromine in aqueous solution, and the reaction appeared to be essentially the same whether the bromine was added rapidly or slowly. We therefore suspended the acid in water, and added at once rather more than two molecules of bromine, taking care to prevent any decided rise of temperature. Carbonic dioxide was slowly evolved, and the red oil which was at first formed gradually solidified. The product was then pressed with filter-paper, and recrystallized from boiling ligroin. Treatment with bone-black was usually necessary in order to obtain a colorless product. The substance thus

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prepared was very readily soluble in alcohol, ether, chloroform, carbonic disulphide, or benzol, more sparingly soluble in ligroin, from which it crystallized in long lustrous prisms which melted at 55–56°. By the slow evaporation of the solution in ligroin quite large and well-developed individuals could be obtained. The substance dried over sulphuric acid gave on analysis the following results: —

I. 0.9663 grm. substance gave 0.5285 grm. CO_2 and 0.0300 grm. H_2O.
II. 0.2053 grm. substance gave 0.3594 grm. AgBr.
III. 0.2344 grm. substance gave 0.4109 grm. AgBr.

	Calculated for $C_4HBr_3O_2$.	Found. I.	II.	III.
C	14.95	14.91		
H	0.31	0.35		
Br	74.76		74.50	74.61

When boiled with water this substance was gradually decomposed, and the aqueous solution then appeared to contain a mixture of dibromsuccinic, monobromfumaric, and monobrommaleic acid, as far as could be determined from the melting-points and other physical properties of the products obtained by evaporation and recrystallization. Since we thought it not improbable that the dibromsuccinic and monobromfumaric acids had been formed from the monobrommaleic acid by the action of the hydrobromic acid formed in the reaction, we decomposed the substance by heating it with a dilute solution of potassic hydrate, added hydrochloric acid in quantity just sufficient to set the organic acid free, extracted with ether, and recrystallized from water the residue left upon evaporation of the ether. In this way we obtained a homogeneous product which melted at 126–127°, and which gave on analysis the percentage of bromine required by monobrommaleic acid.

0.2099 grm. substance gave 0.2013 grm. AgBr.

	Calculated for $C_4H_3BrO_4$.	Found.
Br	41.03	40.82

The chief product of the action of aqueous bromine upon $\beta\delta$-dibrompyromucic acid was therefore monobrommaleyl bromide formed according to the equation,

$$C_5H_2Br_2O_3 + 2\ Br_2 + H_2O = C_4HBr_3O_2 + CO_2 + 3\ HBr.$$

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We have obtained usually about seventy per cent of the theoretical yield of monobrommaleyl bromide, and have been able to isolate no other products of the reaction except such as would naturally result from its decomposition with water.

Action of Nitric Acid.

The $\beta\delta$-dibrompyromucic acid is readily oxidized, with evolution of carbonic dioxide, by boiling even with dilute nitric acid. We have found two parts of strong nitric acid (sp. gr. 1.42), diluted with ten parts of water, sufficient for the complete oxidation of one part of the acid. After the reaction was ended, we extracted the solution with ether and crystallized from water the product obtained by the evaporation of the ether. This product appeared to contain nothing but an acid melting at 174–175°, which on analysis gave the percentage of bromine required by monobromfumaric acid.

0.2254 grm. substance gave 0.2186 grm. AgBr.

	Calculated for $C_4H_3BrO_4$.	Found.
Br	41.03	41.28

Since we have already shown that the product formed by the action of aqueous bromine is a derivative of monobrommaleic acid, we have not hesitated to assume that the first product of the oxidation with nitric acid also is monobrommaleic acid, and that this is converted into monobromfumaric acid by the continued boiling with nitric acid. The reaction may be written,

$$C_5H_2Br_2O_3 + O + H_2O = C_4H_3BrO_4 + CO_2 + HBr.$$

$\beta\gamma$-Dibrompyromucic Acid.

The formation of $\beta\gamma$-dibrompyromucic acid from the pyromucic tetrabromide has already been described, and we have not been able to find any other method for its preparation. For analysis, the acid was recrystallized several times from water, and finally from benzol.

I. 0.6274 grm. substance gave 0.5065 grm. CO_2 and 0.0445 grm. H_2O.
II. 0.2165 grm. substance gave 0.3019 grm. AgBr.
III. 0.2225 grm. substance gave 0.3106 grm. AgBr.

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	Calculated for $C_5H_2Br_2O_3$.	Found. I.	II.	III.
C	22.22	22.02		
H	0.74	0.79		
Br	59.26		59.33	59.40

The $\beta\gamma$-dibrompyromucic acid crystallizes from benzol in short clustered prisms, from water in voluminous feather-like forms. It is readily soluble in ether or alcohol, quite readily soluble in boiling benzol or chloroform, and but sparingly soluble in carbonic disulphide or ligroin. It is rather sparingly soluble even in hot water, and still less soluble in cold water. The solubility of the acid in water at ordinary temperatures we determined by boiling the saturated solution with baric carbonate and precipitating with sulphuric acid the barium dissolved.

I. 53.3668 grm. of a solution saturated at 20° gave 0.0481 grm. $BaSO_4$.
II. 50.6792 grm. of a solution saturated at 20° gave 0.0477 grm. $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the acid: —

I.	II.
0.21	0.22

Baric $\beta\gamma$-Dibrompyromucate, $Ba(C_5HBr_2O_3)_2 . 3 H_2O$. — The barium salt we made by precipitating with baric chloride a dilute ammoniacal solution of the acid, and recrystallizing from boiling water the salt thus precipitated. It formed irregular radiating flattened needles which effloresced over sulphuric acid, but which contained three molecules of water when dried by exposure to the air.

I. 1.6173 grm. of the air-dried salt lost at 150° 0.1226 grm. H_2O.
II. 1.1994 grm. of the air-dried salt lost at 130° 0.0847 grm. H_2O.

	Calculated for $Ba(C_5HBr_2O_3)_2 . 3 H_2O$.	Found. I.	II.
H_2O	7.41	7.58	7.06

I. 1.4947 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.5197 grm. $BaSO_4$.
II. 0.4555 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1544 grm. $BaSO_4$.

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	Calculated for $Ba(C_5HBr_2O_3)_2$.	Found. I.	II.
Ba	20.30	20.44	19.93

The solubility of the salt in cold water we determined by precipitating the saturated solution with sulphuric acid.

I. 41.9064 grm. of a solution saturated at 20° gave 0.0521 grm. $BaSO_4$.
II. 37.7244 grm. of a solution saturated at 20° gave 0.0449 grm. $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

I.	II.
0.36	0.34

Calcic βγ-Dibrompyromucate, $Ca(C_5HBr_2O_3)_2 . 5\,H_2O$. —The calcium salt we made by boiling the acid with water and adding calcic carbonate. The salt recrystallized from boiling water formed concentrically grouped needles, which effloresced slowly in the air, rapidly over sulphuric acid.

I. 1.7504 grm. of the salt lost at 120° 0.2330 grm. H_2O.
II. 2.4934 grm. of the salt lost at 120° 0.3300 grm. H_2O.

	Calculated for $Ca(C_5HBr_2O_3)_2 . 5\,H_2O$.	Found. I.	II.
H_2O	13.47	13.31	13.23

I. 0.5620 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1301 grm. $CaSO_4$.
II. 0.8701 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.2011 grm. $CaSO_4$.

	Calculated for $Ca(C_5HBr_2O_3)_2$.	Found. I.	II.
Ca	6.92	6.81	6.80

The solubility of the salt in water at ordinary temperatures we determined by precipitating a saturated solution with ammonic oxalate, and igniting the calcic oxalate thus obtained with sulphuric acid.

I. 20.5686 grm. of a solution saturated at 20° gave 0.0561 grm. $CaSO_4$.
II. 19.7985 grm. of a solution saturated at 20° gave 0.0538 grm. $CaSO_4$.

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The solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

I.	II.
1.16	1.15

Argentic βγ-Dibrompyromucate, $AgC_5HBr_2O_3$. — From an aqueous solution of the acid argentic nitrate precipitates the silver salt in the form of minute clustered needles, which dissolve without essential decomposition on heating the solution. For analysis we prepared it by precipitating with argentic nitrate a neutral solution of the acid in dilute ammonic hydrate.

0.2584 grm. of the salt gave on precipitation with HBr 0.1297 grm. AgBr.

	Calculated for $AgC_5HBr_2O_3$.	Found.
Ag	28.65	28.83

Sodic βγ-Dibrompyromucate, $NaC_5HBr_2O_3 . 2\,H_2O$. — The sodium salt we prepared by dissolving the acid in a solution of sodic carbonate and recrystallizing from water the salt thus obtained. It formed fine silky needles, which were not very soluble in cold water. The air-dried salt contained two molecules of water.

I. 2.0032 grm. of the air-dried salt lost at 119° 0.2192 grm. H_2O.
II. 1.7440 grm. of the air-dried salt lost at 119° 0.1925 grm. H_2O.

	Calculated for $NaC_5HBr_2O_3 . 2\,H_2O$.	Found. I.	Found. II.
H_2O	10.97	10.94	11.04

I. 0.6162 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1502 grm. Na_2SO_4.
II. 0.6275 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1506 grm. Na_2SO_4.

	Calculated for $NaC_5HBr_2O_3$.	Found. I.	Found. II.
Na	7.88	7.90	7.78

Potassic βγ-Dibrompyromucate, $KC_5HBr_2O_3$. — The potassium salt made by neutralizing the acid with potassic carbonate crystallized in flat clustered prisms, which were not very soluble in cold water and were anhydrous.

I. 0.5082 grm. of the salt gave on ignition with H_2SO_4 0.1390 grm. K_2SO_4.

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II. 0.9303 grm. of the salt gave on ignition with H_2SO_4 0.2603 grm. K_2SO_4.

	Calculated for $KC_5HBr_2O_3$.	Found. I.	II.
K	12.69	12.57	12.56

Ethyl βγ-Dibrompyromucate, $(C_2H_5)C_5HBr_2O_3$. — The ethyl ether we have prepared by the action of ethyl iodide upon the silver salt of the acid, and also by heating the acid in alcoholic solution with concentrated sulphuric acid. For its preparation by the latter method we used the same proportions which we had already found advantageous in the case of the βδ-dibrompyromucic acid; namely, five parts of the acid, five of absolute alcohol, and three of concentrated sulphuric acid. The reaction was completed in a few hours at 100°, and the ether was precipitated with water, washed with a dilute solution of sodic carbonate, and recrystallized from alcohol. Thus prepared, it formed fine silky needles which melted at 67–68°. Its odor recalled at the same time ethyl pyromucate and anise. It is readily soluble in ether, chloroform, benzol, carbonic disulphide, ligroin, or hot alcohol, sparingly soluble in cold alcohol. The material used in Analysis II. was made from the silver salt by the action of ethyl iodide.

I. 0.2193 grm. substance gave 0.2777 grm. AgBr.
II. 0.1497 grm. substance gave 0.1886 grm. AgBr.

	Calculated for $(C_2H_5)C_5HBr_2O_3$.	Found. I.	II.
Br	53.69	53.91	53.62

βγ-Dibrompyromucamide, $C_5HBr_2O_2NH_2$. — Since concentrated aqueous ammonia acted but slowly upon the ethyl βγ-dibrompyromucate in the cold, we heated the mixture in sealed tubes at 100° for several hours. The resulting amide we purified by recrystallization from dilute alcohol. It crystallized from alcohol in fine needles, which melted at 195–196°. It was readily soluble in alcohol, quite sparingly soluble in ether, chloroform, or benzol, and almost insoluble in carbonic disulphide or ligroin. Even in boiling water it was but sparingly soluble.

0.9791 grm. of substance gave 47.0 c.c. of moist nitrogen at 23° under a pressure of 739 mm.

	Calculated for $C_5HBr_2O_2NH_2$.	Found.
N	5.20	5.38

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The $\beta\gamma$-dibrompyromucic acid appears to be incapable of forming an addition product with bromine. When the acid is exposed to an atmosphere of bromine at ordinary temperatures, hydrobromic acid is evolved, and tribrompyromucic acid is formed. This we identified by its melting-point, 218–219°, and by its other physical properties.

Action of Bromine and Water.

Toennies obtained, by the action of bromine water upon the dibrompyromucic acid melting at 186°, a substance to which he assigned the formula $C_4H_2Br_2O_2$, and which he named dibromfumaric aldehyde. He published, however, in the preliminary paper to which we have already alluded,* no analysis of the substance. We have found that the action of aqueous bromine varies greatly, according to the conditions of the reaction; and although we have been able to prepare a substance whose properties nearly correspond to Toennies's description of the dibromfumaric aldehyde, we have not succeeded in making the yield satisfactory. If one molecule of bromine is slowly added by means of a current of air to the acid suspended in water, the color of the bromine gradually disappears, a part of the acid remains unaltered, while a part of it is converted into tetrabromfurfuran. After the solution had become colorless, we collected upon a filter the insoluble product, and washed it with a dilute solution of sodic carbonate. On acidifying the alkaline solution, the unaltered acid melting at 191° was precipitated. The solid insoluble in the solution of sodic carbonate dissolved readily in alcohol, and on cooling crystallized in long needles which melted at 64–65°, and gave on analysis the percentage of bromine required by tetrabromfurfuran.

0.2201 grm. substance gave 0.4319 grm. AgBr.

	Calculated for C_4Br_4O.	Found.
Br	83.33	83.52

A portion of the acid had therefore been decomposed according to the equation,

$$C_5H_2Br_2O_3 + 2\ Br_2 = C_4Br_4O + CO_2 + 2\ HBr.$$

From the aqueous solution which had been filtered from the tetrabromfurfuran and the unaltered acid we obtained by extraction with ether a small quantity of a substance which, when recrystallized from

* Berichte d. deutsch. chem. Gesellsch., xii. 1203.

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dilute alcohol, melted at 89°. This gave on analysis a percentage of bromine which was approximately that required by the formula $C_4H_2Br_2O_2$.

0.1884 grm. substance gave 0.2897 grm. AgBr.

	Calculated for $C_4H_2Br_2O_2$.	Found.
Br	66.12	65.45

The formation of the tetrabromfurfuran could be avoided almost entirely by the rapid addition of the bromine. Still, rather more than one molecule of bromine was necessary for complete oxidation of the acid, and the purification of the product was difficult. The ethereal extract left on evaporation a viscous residue, which rarely solidified when allowed to stand in vacuo over sulphuric acid. By extracting this viscous residue with boiling water, we succeeded, however, in obtaining a crystalline product which melted at 90–91°, but which gave on analysis too low a percentage of bromine (I.). Since it seemed not improbable that the substance contained mucobromic acid, we dissolved it in a dilute solution of sodic carbonate, and extracted it from the alkaline solution with ether; but the percentage of bromine was unaltered (II.). By sublimation in a stream of carbonic dioxide, however, we obtained a product which melted at 89–90°, and gave the required percentage of bromine (III.).

I. 0.1496 grm. substance gave 0.2295 grm. AgBr.
II. 0.1981 grm. substance gave 0.2955 grm. AgBr.
III. 0.1340 grm. substance gave 0.2089 grm. AgBr.

	Calculated for $C_4H_2Br_2O_2$.	Found.		
		I.	II.	III.
Br	66.12	63.57	63.48	66.36

This substance is readily soluble in alcohol, ether, chloroform, or benzol, more sparingly soluble in ligroin. It is readily soluble in hot water, more sparingly in cold, and crystallizes from aqueous solution in small prisms which often form lattice-like aggregations. By oxidation it yields mucobromic acid, and it must therefore be considered to be dibrommaleic aldehyde. The difficulty of its preparation in quantity made it impossible for us to study it more in detail at present, but we hope to return to it at some future time.

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Action of Nitric Acid.

Dilute nitric acid oxidizes the $\beta\gamma$-dibrompyromucic acid readily on heating. Carbonic dioxide is given off, and the solution then contains mucobromic and dibrommaleic acids. Toennies's erroneous statement that his acid was with difficulty oxidized even by strong nitric acid was doubtless due to the fact that but little hydrobromic acid is formed by the oxidation. For the complete oxidation of the acid we have found two parts of strong nitric acid (sp. gr. 1.42) diluted with five times its weight of water sufficient. After the reaction was over, we extracted with ether and treated the white crystalline residue left on evaporation of the ether with small quantities of cold water. The sparingly soluble mucobromic acid was thus left undissolved, and its identity proved by its melting-point (120–121°) and by analysis.

0.2040 grm. substance gave 0.2967 grm. AgBr.

	Calculated for $C_4H_2Br_2O_3$.	Found.
Br	62.02	61.90

The strongly acid aqueous solution was evaporated to dryness and the residue again treated with a small amount of cold water, in order to insure the removal of the mucobromic acid. The solution thus obtained was neutralized with baric carbonate, the barium salt precipitated with alcohol and recrystallized from water. The air-dried salt then proved to contain a percentage of barium, agreeing with that required by baric dibrommaleate.

0.5138 grm. of the air-dried salt gave on ignition with H_2SO_4 0.2691 grm. $BaSO_4$.

	Calculated for $BaC_4Br_2O_4 . 2\,H_2O$.	Found.
Ba	30.78	30.80

The acid obtained from this barium salt was converted into its anhydride by sublimation, and its identity with dibrommaleic anhydride was shown by its melting-point, 114–115°.

The oxidation of $\beta\gamma$-dibrompyromucic acid with dilute nitric acid may therefore be expressed by the equations,

$$C_5H_2Br_2O_3 + 2\,O = C_4H_2Br_2O_3 + CO_2.$$
$$C_5H_2Br_2O_3 + 3\,O = C_4H_2Br_2O_4 + CO_2.$$

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Tribrompyromucic Acid.

Tribrompyromucic acid can readily be made from δ-monobrompyromucic tetrabromide by the action of an alcoholic solution of sodic hydrate. Although, as has already been remarked, this acid is formed through secondary reactions in the preparation of the dibrompyromucic acids from pyromucic tetrabromide, we have obtained in this way but a small quantity of the acid, and have prepared most of the material we have needed for the investigation from monobrompyromucic acid. The formation of the tribrompyromucic acid by the action of bromine upon the βγ-dibrompyromucic acid has already been noticed. Since the hydrogen of the isomeric dibrompyromucic acid cannot be directly replaced by bromine, tribrompyromucic acid cannot be made by the direct action of bromine upon pyromucic acid.

In the decomposition of the monobrompyromucic tetrabromide we have found a low temperature and a concentrated solution of sodic hydrate advantageous. The sodium salt of the tribrompyromucic acid is but sparingly soluble in alcohol, and may be separated by filtration. The alcoholic mother-liquors proved to contain a substance insoluble in water and readily volatile with the vapor of alcohol. For its isolation we precipitated the excess of sodic hydrate with carbonic dioxide, distilled the filtered solution, and precipitated the distillate by the addition of water. The heavy oil which was thus thrown down we dried with calcic chloride, and submitted it to fractional distillation in an atmosphere of carbonic dioxide under diminished pressure. After several distillations, by far the greater portion of the oil showed the constant boiling-point 96–98° under a pressure of 20 mm., and we were unable to isolate other definite products. An analysis showed the main product to be a tribromfurfuran.

0.3417 grm. substance gave 0.6299 AgBr.

	Calculated for C_4HBr_3O.	Found.
Br	78.68	78.39

Tribromfurfuran had, therefore, been formed from the monobrompyromucic tetrabromide according to the equation,

$$C_5H_3Br_5O_3 = C_4HBr_3O + CO_2 + 2\,HBr.$$

The sodium salt which had separated from the alcoholic solution we acidified with hydrochloric acid, and recrystallized the acid thus obtained from dilute alcohol, and finally from water.

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I. 0.6837 grm. substance gave 0.4266 grm. CO_2 and 0.0221 grm. H_2O.
II. 0.1658 grm. substance gave 0.2684 grm. AgBr.
III. 0.1885 grm. substance gave 0.3047 grm. AgBr.

	Calculated for $C_5HBr_3O_3$.	Found. I.	II.	III.
C	17.20	17.02		
H	0.28	0.36		
Br	68.77		68.90	68.79

Tribrompyromucic acid crystallizes in minute clustered needles which melt at 218–219°. It is readily soluble in alcohol or ether, somewhat sparingly soluble in chloroform or benzol, and very sparingly soluble in carbonic disulphide or ligroin. It dissolves with difficulty even in boiling water, and the hot solution deposits the greater part of the acid on cooling. In order to determine the solubility of the acid in cold water, we boiled the saturated solution with baric carbonate and precipitated with sulphuric acid the barium dissolved.

I. 43.8259 grm. of a solution saturated at 19° gave 0.0105 grm. $BaSO_4$.
II. 42.6017 grm. of a solution saturated at 19° gave 0.0101 grm. $BaSO_4$.

According to these determinations the aqueous solution saturated at 19° contained the following percentages of the acid: —

I.	II.
0.072	0.071

Baric Tribrompyromucate, $Ba(C_5Br_3O_3)_2 . 3\,H_2O$.—The barium salt we prepared by precipitating a solution of baric chloride with a solution of the acid in dilute ammonic hydrate and recrystallizing from boiling water the salt thus obtained. It crystallized in dendritic needles, which, when air-dried, contained three molecules of water, nearly all of which it lost over sulphuric acid.

I. 1.1629 grm. of the salt lost at 120° 0.0695 grm. H_2O.
II. 1.6160 grm. of the salt lost at 120° 0.0970 grm. H_2O.

	Calculated for $Ba(C_5Br_3O_3)_2 . 3\,H_2O$.	Found. I.	II.
H_2O	6.09	5.98	6.00

I. 0.6867 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1878 grm. $BaSO_4$.

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II. 0.8009 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.2192 grm. $BaSO_4$.

	Calculated for $Ba(C_5Br_3O_3)_2$.	Found. I.	II.
Ba	16.44	16.08	16.07

The solubility of the salt in cold water we determined by precipitating the saturated solution with sulphuric acid.

I. 36.2176 grm. of a solution saturated at 20° gave 0.0197 grm. $BaSO_4$.
II. 32.6167 grm. of a solution saturated at 20° gave 0.0181 grm. $BaSO_4$.

The aqueous solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt: —

I.	II.
0.19	0.20

Calcic Tribrompyromucate, $Ca(C_5Br_3O_3)_2 . 4H_2O$. — The calcium salt we prepared by precipitating an ammoniacal solution of the acid with calcic chloride. When recrystallized from hot water, it formed clusters of fine dendritic needles, which were permanent in the air, but effloresced over sulphuric acid.

I. 1.5509 grm. of the salt lost at 120° 0.1385 grm. H_2O.
II. 0.9115 grm. of the salt lost at 120° 0.0799 grm. H_2O.

	Calculated for $Ca(C_5Br_3O_3)_2 . 4\,H_2O$.	Found. I.	II.
H_2O	8.91	8.93	8.77

I. 0.5885 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1060 grm. $CaSO_4$.
II. 0.6364 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1122 grm. $CaSO_4$.

	Calculated for $Ca(C_5Br_3O_3)_2$.	Found. I.	II.
Ca	5.44	5.30	5.18

In order to determine the solubility of the salt in cold water, we precipitated the saturated solution with ammonic oxalate, and converted the calcic oxalate thus obtained into calcic sulphate by ignition with sulphuric acid.

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I. 34.5554 grm. of a solution saturated at 20° gave 0.0346 grm. $CaSO_4$.

II. 27.6386 grm. of a solution saturated at 20° gave 0.0267 grm. $CaSO_4$.

The aqueous solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt: —

I.	II.
0.54	0.57

Argentic Tribrompyromucate, $AgC_5Br_3O_3$. — Argentic nitrate gives even in the cold aqueous solution of the acid a crystalline precipitate of the silver salt, which is sparingly soluble even in boiling water. It may readily be prepared by precipitating a soluble salt of the acid with argentic nitrate and washing with hot water.

0.2977 grm. of the salt gave 0.1242 grm. AgBr.

	Calculated for $AgC_5Br_3O_3$.	Found.
Ag	23.68	23.96

Sodic Tribrompyromucate, $NaC_5Br_3O_3 . H_2O$. — The sodium salt we prepared by dissolving the acid in a dilute solution of sodic carbonate. The salt was not very soluble in cold water, and crystallized, on cooling the aqueous solution, in fine woolly needles, which contained one molecule of water and slowly effloresced over sulphuric acid.

I. 1.0434 grm. of the air-dried salt lost at 108° 0.0457 grm. H_2O.

II. 1.1171 grm. of the air-dried salt lost at 112° 0.0531 grm. H_2O.

	Calculated for $NaC_5Br_3O_3 . H_2O$.	Found. I.	Found. II.
H_2O	4.63	4.38	4.76

I. 0.5947 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1132 grm. Na_2SO_4.

II. 0.5036 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.0987 grm. Na_2SO_4.

	Calculated for $NaC_5Br_3O_3$.	Found. I.	Found. II.
Na	6.20	6.17	6.35

Potassic Tribrompyromucate, $KC_5Br_3O_3 . H_2O$. — The potassium salt we prepared by neutralizing a dilute solution of potassic carbonate with the acid. It was not very soluble in cold water, and crystallized,

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on cooling the aqueous solution, in globular aggregations of fine needles. The air-dried salt contained one molecule of water and slowly effloresced over sulphuric acid.

I. 1.6850 grm. of the air-dried salt lost at 120° 0.0753 grm. H_2O.
II. 1.7346 grm. of the air-dried salt lost at 112° 0.0784 grm. H_2O.

	Calculated for $KC_5Br_3O_3 . H_2O$.	Found. I.	II.
H_2O	4.44	4.47	4.52

I. 0.6838 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1522 grm. K_2SO_4.
II. 0.5826 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.1319 grm. K_2SO_4.

	Calculated for $KC_5Br_3O_3$.	Found. I.	II.
K	10.10	10.09	10.16

Ethyl Tribrompyromucate, $(C_2H_5)C_5Br_3O_3$.— The ethyl ether we have prepared by warming the silver salt of the acid with ethyl iodide, and also by heating an alcoholic solution of the acid with concentrated sulphuric acid. In the latter case we found it convenient to use two parts of absolute alcohol and one part of concentrated sulphuric acid to one part of the acid. After heating for several hours at 100°, we precipitated the ether by the addition of water, washed it with a dilute solution of sodic carbonate, and recrystallized it from alcohol. It formed clear rectangular prisms, which melted at 104°, and have little or no odor at ordinary temperatures. It is readily soluble in ether, chloroform, benzol, or carbonic disulphide, somewhat more sparingly soluble in ligroin. It is quite sparingly soluble even in boiling alcohol. The material used in Analysis II. was made from the silver salt.

I. 0.1785 grm. substance gave 0.2677 grm. AgBr.
II. 0.1526 grm. substance gave 0.2284 grm. AgBr.

	Calculated for $(C_2H_5)C_5Br_3O_3$.	Found. I.	II.
Br	63.66	63.83	63.71

Tribrompyromucamide, $C_5Br_3O_2NH_2$. — Although ethyl tribrompyromucate is but slowly attacked by concentrated aqueous ammonia at ordinary temperatures, it is readily decomposed at 100° in sealed tube with the formation of tribrompyromucamide. The resulting product was purified by recrystallization from alcohol, and formed then fine

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needles which melted at 222–223°. It was readily soluble in hot alcohol, quite sparingly soluble in ether, chloroform, or benzol, insoluble in carbonic disulphide or ligroin. It was nearly insoluble even in boiling water.

0.6792 grm. substance gave 23.5 c.c. of moist nitrogen at 22° and under a pressure of 744 mm.

	Calculated for $C_5Br_3O_2NH_2$.	Found.
N	4.02	3.92

Action of Bromine and Water.

Bromine acts but slowly upon tribrompyromucic acid suspended in water, and even if the acid be finely subdivided a portion of it escapes decomposition. Since little action was visible when the vapor of bromine was slowly led in by means of a current of air, we added exactly one molecule of bromine, and then collected upon a filter the insoluble matter which remained. A portion of this dissolved in a dilute solution of sodic carbonate, and could be reprecipitated by the addition of hydrochloric acid. The properties of the precipitated acid and its melting-point (216°) showed it to be unaltered tribrompyromucic acid. The portion which was insoluble in the alkaline solution was dissolved in boiling alcohol, and on cooling crystallized in long slender needles which melted at 63–64°. An analysis gave the percentage of bromine required by tetrabromfurfuran.

0.2217 grm. substance gave 0.4359 grm. AgBr.

	Calculated for C_4Br_4O.	Found.
Br	83.33	83.68

The aqueous solution filtered from the tetrabromfurfuran and the unaltered tribrompyromucic acid yielded, on extraction with ether, dibrommaleic acid in quantity too small to admit of analysis, although its identity could readily be established by the melting-point of its anhydride (114–115°). With aqueous bromine, therefore, tribrompyromucic acid yields essentially tetrabromfurfuran and carbonic dioxide according to the equation,

$$C_5HBr_3O_3 + Br_2 = C_4Br_4O + CO_2 + HBr.$$

Action of Nitric Acid.

Tribrompyromucic acid is much less readily attacked by dilute nitric acid than either of the dibrompyromucic acids, and to effect its oxida-

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tion we were obliged to use three parts of strong nitric acid (sp. gr. 1.42) diluted with twice its weight of water to one part of the acid. After continued boiling the acid was dissolved, and from the clear solution, by extraction with ether, we were able to isolate only dibrommaleic acid, which melted at 125°, and gave by sublimation an anhydride which melted at 114–115°. The barium salt was prepared by neutralizing the acid in aqueous solution with baric carbonate, and precipitating the filtered solution with alcohol. This salt, when recrystallized from water and dried by exposure to the air, gave the percentage of barium required by baric dibrommaleate.

0.5259 grm. of the air-dried salt gave on ignition with H_2SO_4 0.2765 grm. $BaSO_4$.

	Calculated for $BaC_4Br_2O_4 . 2\,H_2O$.	Found.
Ba	30.78	30.91

By the oxidation of tribrompyromucic acid with nitric acid dibrommaleic acid is, therefore, formed according to the equation,

$$C_5HBr_3O_3 + 2\,O + H_2O = C_4H_2Br_2O_4 + CO_2 + HBr.$$

Theoretical Considerations.

It is evident that definite conclusions as to the relative position of the bromine atoms in the various substituted pyromucic acids which we have described may be drawn from the products which result from the oxidation, and at the same time it seems to us that certain of our observations enable us to discriminate between the two structure formulæ for pyromucic acid which have hitherto seemed most probable. The behavior of pyromucic acid with phosphorus pentachloride, as shown by the experiments of Liès-Bodart,* or of its ethyl ether with acetyl chloride, as shown by Schmelz and Beilstein,† rendered it certain that pyromucic acid could not contain its third oxygen atom in the form of hydroxyl. Limpricht's ‡ experiments with furfuran (tetraphenol), and the indifference shown by pyromucic acid toward nascent hydrogen, excluded the possibility of the presence of an aldehyde or ketone group. The absence of both of these forms of oxygen has more recently been confirmed by the experiments of Odernheimer,§

* Ann. Chem. u. Pharm., c. 327.

† Ibid., Suppl., iii. 276.

‡ Ibid., clxv. 282.

§ Ber. der deutsch. chem. Gesell., xvi. 2988.

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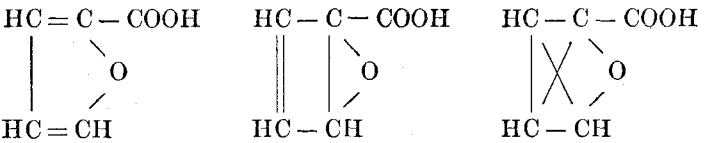
who showed that pyromucic acid was not attacked by hydroxylamine, and of Wagner,* who failed to reduce the furfuran oxygen with zinc ethyl. Of the known forms in which oxygen occurs, therefore, there remains only the oxide form, C-O-C, which can be assumed to exist in the molecule of pyromucic acid. Moreover, Baeyer † has shown by the conversion of furfurol into furfuracrylic, furfurpropionic, furonic, and pimelic acids that the carboxyl group of the pyromucic acid is attached directly to one of these two carbon atoms which bear the oxygen atom.

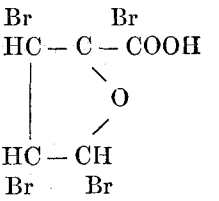
In accordance with these facts, Baeyer has proposed the following three formulæ for pyromucic acid, the first of which he suggested in 1870,‡ the other two in 1877 §:—



1. 2. 3.

Of these three formulæ, however, Baeyer preferred the second, since it appeared to explain most readily the formation from pyromucic acid of derivatives of fumaric acid which Limpricht had observed.

Since pyromucic acid forms an addition product containing four atoms of bromine, to this tetrabromide must be assigned in any case one and the same formula.



The simultaneous formation from this tetrabromide of two dibrompyromucic acids, which we have observed, one of which can be converted by oxidation into monobromfumaric (or monobrommaleic) acid, the second into dibrommaleic (or mucobromic) acid, seems to us to necessitate the rejection of the second formula. From the pyromucic

* Ber. der deutsch. chem. Gesell., xvii. 1967.
† Ibid., x. 1358. ‡ Ibid., iii. 517. § Ibid., x. 1361.

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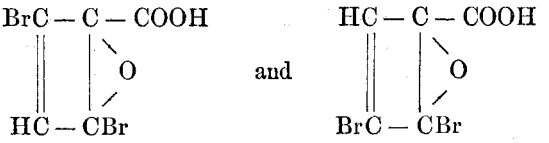
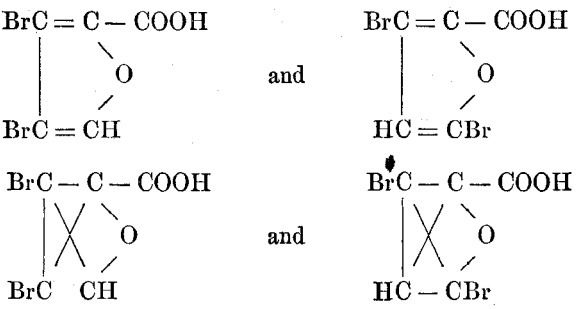
tetrabromide whose formula is given above two isomeric dibrompyromucic acids can in any case be formed; but if the second formula for pyromucic acid be adopted, these would necessarily have the structure,



both of which would yield on oxidation monobromfumaric or monobrommaleic acid. On the other hand, the adoption of either the first or the third formula for pyromucic acid would give for the resulting dibrompyromucic acids the forms,



In either case, the oxidation products which we have observed would find in these formulæ a natural explanation.

While either of these two formulæ will explain the facts which we have observed, it seems to us that there can be no doubt that preference should be given to the first. Aside from the difficulty of explaining by means of the third formula the formation of the pyromucic tetrabromide, and the re-establishment of the carbon ties by the action of caustic alkalies, the formation of Heintzlemann's dehydromucic acid from mucic acid, which certainly is a dicarboxyfurfuran, would necessitate the assumption of a mode of dehydration in whose support, so far as we are aware, no analogous cases can be advanced. On the other hand, the ready formation of the lactones, as shown by the brilliant researches of Fittig, renders the formation of a stable oxide by the elimination of water involving hydroxyl groups attached to the first and fourth carbon atoms a matter in every way probable. We cannot deny that the adoption of the first formula renders the

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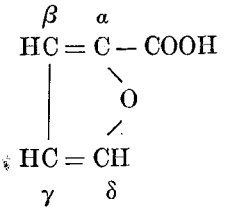
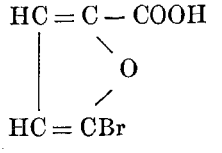
explanation of the formation of derivatives of fumaric or maleic acid by oxidation somewhat difficult (the same objection applies, of course, to a still greater degree to the third formula); and still we cannot consider this objection a serious one, while the normal behavior of substances containing the group C=C-C=C is not established, and the ease with which molecular rearrangements take place in non-saturated compounds is so well known. Until the structure of fumaric and maleic acids is more definitely established, it would be useless to attempt any discussion of the significance of the fact which we have established, that maleic acid and its derivatives, and not the corresponding derivatives of fumaric acid, are the first products formed in the decomposition of the substituted pyromucic acids.

If the carbon atoms in pyromucic acid are designated as usual, beginning with the carboxyl group,



the constitution of the two isomeric dibrompyromucic acids may be expressed by the names which we have given to them, the $\beta\gamma$-dibrompyromucic acid (melting-point 191–192°), passing by oxidation into dibrommaleic acid, while the $\beta\delta$-dibrompyromucic acid yields monobrommaleic acid.

The determination of the constitution of the monobrompyromucic acids is a matter of no difficulty. The oxidation of the monobrompyromucic acid melting at 183–184° directly to maleic or fumaric acid shows that its bromine must be in the δ-position, and its formula,



On the other hand, the monobrompyromucic acid melting at 128–129°, since it is formed by the reduction of either of the two dibrompyromucic acids, must have its bromine atom at β, and its formula is therefore

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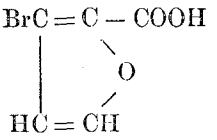
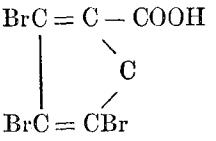


By oxidation with nitric acid it gives, as it should, monobromfumaric acid.

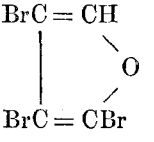
Since all the furfuran hydrogens are replaced by bromine in tribrompyromucic acid, but one form of the acid is possible, and that is



Of the substituted pyromucic acids which we have studied, those which contain a bromine atom in the δ-position give, by oxidation with bromine water, dibasic acids, while those in which the δ-hydrogen is not thus replaced yield ultimately the aldehyde acid, mucobromic acid. Although we are unable to follow at present the successive steps by which this oxidation proceeds, it may fairly be inferred that the α-carbon atom is in any case completely oxidized, while the δ-carbon atom appears in the aldehyde group whenever this is formed.

The strong analogies between the derivatives of furfuran and of benzol have frequently been pointed out during the past few years. It is interesting to note that by the action of bromine upon pyromucic acid the δ and β hydrogen atoms are successively replaced. If the group CH=CH be substituted for the oxygen of furfuran, these become respectively the para and ortho positions of the aromatic series. While benzoic acid itself is converted into metabrombenzoic acid by the action of bromine, the formation of para and ortho derivatives under these conditions is more frequently observed in the aromatic series.

While we, unfortunately, have been able as yet to obtain no direct evidence as to the constitution of the substituted furfurans which we have described, there can be little doubt as to their structure. The tribromfurfuran obtained in the preparation of tribrompyromucic acid must certainly have the formula



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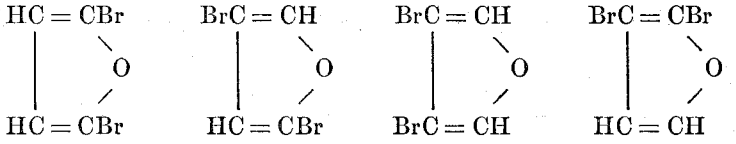
and the tribromfurfuran obtained from the crude pyromucic tetrabromide is undoubtedly identical with it.

Of the four formulæ for dibromfurfuran, which are possible if the formulæ of furfuran we have adopted be correct,



1. 2. 3. 4.

the first undoubtedly represents the structure of a dibromfurfuran which has already been described in a preliminary paper by Mr. George T. Hartshorn and one of us.* The mode of its formation, and its reactions, leave no possible doubt as to its constitution. It seems to us that there can be no reasonable doubt that the two dibromfurfurans which we have just described must have the structure represented by the second and third formulæ, corresponding to the formulæ of the two dibrompyromucic acids formed at the same time. The latter formula, then, probably represents the more stable substance of lower boiling-point.

* Ber. der deutsch. chem. Gesell., xviii. 448

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VI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF CHROMIC SUPERFLUORIDE ON BENZOIC ACID.

By C. Loring Jackson and George T. Hartshorn.

Communicated May 13, 1885.

As the chromic superfluoride is instantly decomposed by water with the formation of chromic anhydride and hydrofluoric acid, we undertook the experiments described in the following paper in the hope that organic compounds containing hydroxyl would act in a similar way; and since Mallet's* determination of the vapor-density of hydrofluoric acid obliges us to assign it the formula H_2F_2, that thus we might obtain organic substances, in which the oxygen of the hydroxyl was replaced by two atoms of fluorine, as in fluosilicic acid. This hope has not been realized in the case of benzoic acid, with which we began our experiments, as the chromic superfluoride left the hydroxyl entirely unaltered; but, on the other hand, it has led us to a very interesting result, as the products of the reaction were chromic fluoride (Cr_2F_6) and a difluorbenzoic acid, and therefore we have achieved for the first time, so far as we can find, the direct substitution of the hydrogen in an organic substance by fluorine. Preliminary experiments with acetic acid and benzol seem to show that the reaction is a general one, — in both cases the chromic superfluoride was reduced to a lower fluoride of chromium, — and there is good promise, therefore, that it will prove of service in adding new members to the class of fluorine organic compounds, as yet so meagrely represented.

We have not made a complete study of the difluorbenzoic acid, but have contented ourselves with doing enough to characterize it thoroughly, as we are anxious to avoid any interference with Paterno, who has already begun the investigation of organic bodies in which

* Am. Chem. J., iii. 189.

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hydrogen is replaced by fluorine. Nor do we intend to continue our experiments on acetic acid and benzol, as Paterno has announced that he is at work on the fluorine derivatives of both these substances. We wish, however, to reserve for our future study the action of chromic superfluoride on all other organic substances.

The remainder of the paper consists of the detailed account of our experimental work.

Action of Chromic Superfluoride on Benzoic Acid.

The chromic superfluoride was made by the action of 180 gr. of fuming sulphuric acid on 60 gr. of potassic dichromate and 100 gr. of calcic fluoride, both of which must be perfectly dry. If the fuming sulphuric acid is very strong, it should be diluted with ordinary strong sulphuric acid, as, if this precaution is neglected, the action is so violent that it cannot be controlled, a large amount of the superfluoride is wasted, and in extreme cases the cover may be blown off the lead retort. The lead retort used was of the cylindrical form figured in most text-books for making the aqueous solution of hydrofluoric acid; the fuming sulphuric acid was first introduced, the fluor-spar and potassic dichromate previously thoroughly mixed were then added, and stirred in with an iron rod, the cover put on, and the reaction started by a gentle heat. As soon as faint white fumes appear at the exit tube, the lamp should be removed, and, after the first violent evolution of gas has slackened, the action can be made to proceed smoothly by a gentle heat, although it is hard to avoid occasional rushes of gas. It is hardly necessary to say that the work should be carried on under a good hood, and the hands protected by india-rubber gloves. After the process is finished, the retort should be emptied before it has become cold, as after the residue has hardened its removal is both difficult and tedious.

The chromic superfluoride obtained in this way is not free from hydrofluoric acid, to judge from the white fumes which were observed mixed with the dark red heavy vapor; but it was pure enough for our purpose, and was allowed to act directly on the solid benzoic acid, which was spread in a layer rather less than a centimeter thick over the bottom of a platinum dish, or on its cover; for this purpose the lead pipe, which formed the exit tube of the retort, was brought down so that it nearly touched the surface of the acid. Absolute contact must be avoided, as in this case the tube soon becomes stopped up with the fused product. With a rapid stream of the superfluoride the action

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is vigorous, the benzoic acid fusing and forming a black crust, which was made to spread over the whole surface by moving the dish when necessary; the crust was then removed,* and the same action repeated with fresh benzoic acid, until all the superfluoride was exhausted. In this way 180 gr. of the crusts could be obtained in a single operation. If the stream of superfluoride was not rapid, the benzoic acid was apt to become covered with chromic anhydride, probably from a trace of moisture in the acid, and this not infrequently gave rise to unimportant deflagrations; but the amount of chromic anhydride formed even by this secondary reaction is very small, almost the whole of the chromic superfluoride being converted directly into the green chromic fluoride Cr_2F_6.

To obtain the difluorbenzoic acid from the crude product it was dissolved in a strong solution of sodic carbonate, and, after the chromic hydrate had been removed by filtration, fractionally precipitated with hydrochloric acid, the liquid being boiled with the separated benzoic acid after each precipitation. We found it wisest to divide the whole into two about equal fractions at first, and then to fraction the least acid portion again, when all the difluorbenzoic acid collected in the least acid fraction, which should be made very small; this was then boiled with water, and the residue purified by recrystallization from boiling benzol and sublimation. The yield of difluorbenzoic acid is only 1.5 per cent of the benzoic acid used.

Having obtained the difluorbenzoic acid, we next tried to detect the presence of monofluorbenzoic acid, and for this purpose examined the acid contained in the hot aqueous filtrate from boiling the difluor acid with water, and also the fraction immediately preceding the least acid one. As the metafluorbenzoic acid melts at 123°–124° according to Paterno and Oliveri,† the melting-point was of no assistance to us, and we have accordingly made a number of analyses of the barium salts of these fractions, both before and after a repetition of the fractional saturation, which have given results varying from 35.81 to 35.99 per cent of barium; baric benzoate contains 36.15 per cent, baric fluorbenzoate 33.01 per cent.‡ We also thought it might be contained in a mixture of acids, obtained by boiling the crude product with insufficient water, melting sometimes as low as 102°; but this on fractional neutralization

* We think it right to mention that both of us were poisoned, one severely, by the crude product, which was spilt on our clothes in removing the crusts from the platinum dishes.

† Ber. d. ch. G., 1882, p. 1197.

‡ The most acid fractions were also pure benzoic acid, as was to be expected.

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was divided into difluorbenzoic acid and benzoic acid, as proved by analyses of the barium salt. We are convinced, therefore, that no monofluorbenzoic acid is formed by the action of chromic superfluoride on benzoic acid, but the products of the reaction are only difluorbenzoic acid and chromic fluoride with a little chromic anhydride as an impurity.

Difluorbenzoic Acid, $C_6H_3F_2COOH$.

The acid prepared and purified, as described above, appears when sublimed in white flattened needles looking very much like benzoic acid, when crystallized from alcohol or benzol in short fine needles; it sublimes at a temperature far below its melting-point, 232° (uncor.), but with much more difficulty than benzoic acid, and burns with a strongly green-bordered flame. It is essentially insoluble in cold water, and only slightly soluble in hot, the boiling solution depositing a few crystalline flocks of the acid on cooling; not very freely soluble in cold alcohol or benzol, but freely in either of these solvents when hot, very soluble in ether or glacial acetic acid, less so in methyl alcohol, and almost insoluble in ligroine, or carbonic disulphide. Benzol is the best solvent for purifying it by crystallization.

Its composition was established by the following combustions: —

I. 0.2549 gr. of substance burnt with plumbic chromate in a closed tube* gave 0.4964 gr. of carbonic dioxide and 0.0982 gr. of water.

II. 0.1595 gr. gave 0.3131 gr. of carbonic dioxide and 0.0506 gr. of water.

	Calculated for $C_7H_4F_2O_2$.	Found. I.	II.
Carbon	53.16	53.13	53.52
Hydrogen	2.53	4.28	3.53

The ammonic difluorbenzoate is decomposed by evaporating its solution to dryness; but a solution freed from ammonia by boiling gave white precipitates with plumbic acetate, and mercurous, mercuric, and argentic nitrates, and a bluish white precipitate with cupric sulphate.

Baric Difluorbenzoate, $Ba(C_7H_3F_2O_2)_2$, made by boiling the acid with baric carbonate and water, crystallizes in white scales, and contains no water of crystallization even when only air-dried.

* We found it impossible to obtain agreeing results when the combustion was performed in the ordinary way with oxygen.

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I. 0.2716 gr. of the salt dried at 110° gave 0.1395 gr. of baric sulphate.

II. 0. 2674 gr. gave 0.1378 gr. of baric sulphate.

	Calculated for $Ba(C_7H_3F_2O_2)_2$.	Found. I.	II.
Barium	30.38	30.20	30.28

Its solubility in water was determined according to the method of Victor Meyer: —

I. 1.5814 gr. of a solution saturated at 15° gave 0.0188 gr. of the salt by evaporation.

II. 2.6260 gr. gave 0.0310 gr. of the salt.

Therefore, the solution saturated at 15° contains the following percentages of the salt: —

I.	II.
1.19	1.18

Calcic Difluorbenzoate, $Ca(C_7H_3F_2O_2)_2 . 3\ H_2O$.

This very characteristic salt, made by boiling the acid with calcic carbonate and water, begins to crystallize out, as soon as the liquid is somewhat concentrated, in bundles of silky needles, frequently a centimeter long, and slightly branched at a very acute angle.

I. 0.7886 gr. of the air-dried salt lost 0.1058 gr. at 100°.

II. 0.3605 gr. lost 0.0495 gr.

	Calculated for $Ca(C_7H_3F_2O_2)_2 . 3\ H_2O$.	Found. I.	II.
Water	13.28	13.42	13.73

I. 0.2440 gr. of the salt dried at 100° gave 0.0914 gr. of calcic sulphate.

II. 0.3024 gr. gave 0.1153 gr. of calcic sulphate.

	Calculated for $Ca(C_7H_3F_2O_2)_2$.	Found. I.	II.
Calcium	11.30	11.02	11.21

Its solubility in water was determined according to the method of Victor Meyer: —

I. 2.0134 gr. of a solution saturated at 15° gave 0.0100 gr. of the anhydrous salt by evaporation.

II. 5.1731 gr. gave 0.0256 gr. of the anhydrous salt.

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Therefore, the solution saturated at 15° contains the following percentages of the anhydrous salt.

I.	II.
0.50	0.49

The calcium salt when heated with an excess of lime gives off a combustible vapor, probably difluorbenzol, as only 4 per cent of fluorine was removed from the acid in this way, but we do not intend to try to isolate this product for fear of interfering with Paterno. This observation was made in an attempt to determine the fluorine in the acid by Piria's method,* which showed that a much larger layer of alkali than could be obtained in this way was needed to remove the fluorine from the organic compound. We propose in our subsequent work to make another effort to solve this difficult problem in organic analysis.

It is to be observed that the large percentages of hydrogen obtained in the combustion of the acid correspond to the formula $C_6H_5F_2CO_2H$ better than to $C_6H_3F_2CO_2H$, and that our other analytical work is not capable of deciding between these formulas. The formula $C_6H_5F_2CO_2H$ would be that of an oxybenzoic acid containing two atoms of fluorine instead of one of oxygen $\left(\begin{matrix}C_6H_4COOH\\F_2H\end{matrix}\right)$, and although the difficulty of removing the fluorine from the acid rendered this formula highly improbable, we have thought it necessary to prove that it was incorrect. For this purpose we treated the acid with a large excess of potassic hydrate in alcoholic solution, and analyzed the potassium salt, which can be precipitated by ether in broad silvery scales, when we obtained an amount of potassium corresponding to the formula $C_6H_3F_2CO_2K$.

* H. Schiff, Ann. Chem., cxcv. 293.

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VII.

ON THE INFLUENCE OF MAGNETIC STRESS UPON THE CAPACITY OF AN ELECTRIC CONDENSER.

By A. S. Kimball.

Communicated June 10, 1885.

Recent work in the laboratory of the Worcester Institute of Industrial Science has apparently established results of which the following is a brief statement.

When an electric condenser placed between the poles of a powerful electro-magnet is charged and discharged through a galvanometer, its capacity as indicated by the swing of the needle is increased by the excitement of the magnet, if its lines of force are perpendicular to the plates of the condenser; but if the condenser plates are parallel to these lines, the capacity is diminished. The percentages of increase in one case and decrease in the other are equal in magnetic fields of the same intensity, and these variations from the normal capacity are greater as the intensity of the field increases.

The experiments which led to these conclusions were suggested by Maxwell's statements, which indicate a similarity of stress existing in the electro-static and electro-magnetic fields. Maxwell also says that in a field on which electro-static as well as electro-magnetic action is taking place, we must suppose the one stress superposed on the other.

Several methods of experiment were successively tried, and rejected on account of possible sources of error, before the final disposition of apparatus was reached.

The first trial was with a $\frac{1}{2}$ microfarad condenser placed on edge between the poles of an electro-magnet. The cores of the magnet were 2 inches in diameter and 13 inches long, and were united by a massive soft iron yoke. Each branch was wound with 275 convolutions of wire through which a current of 11 ampères was driven by a dynamo, about ten feet distant. Movable pole pieces were used, and by varying their distance from each other the intensity of the magnetic field could be increased or diminished at will. The current from the dynamo

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measured by a large tangent galvanometer was approximately constant during the whole series of experiments.

This apparatus was placed in a basement about sixty feet from the testing-table on the floor above. A pair of carefully insulated wires made connection between the condenser and the testing-table. On the table was a Thomson reflecting galvanometer of 7,000 ohms resistance, and the charging key. A water battery was used to charge the condensers, and the charging potential varied at need from 3 to 175 volts.

The $\frac{1}{2}$ microfarad condenser was charged and discharged through a plain key, the magnet being alternately excited and inactive.

Encouraging but not decisive indications were obtained. The variation was so small a part of the total capacity, that it was masked by errors of experiment and observation.

To reduce the deflection of the needle to a manageable amount and yet retain the same variation, if any, a new condenser of about the same capacity was made, and three keys used. By the first, both condensers were charged simultaneously to the same potential; by the second, they were discharged into each other; and by the third, the difference between their charges was discharged through the galvanometer.

The use of three keys was found to introduce great errors, arising from variations in the time given to each of the operations mentioned above, and a new key was made which required but a single motion instead of three. After adopting a uniform time of charging — in the majority of cases fifteen seconds — fairly constant results were obtained, and some of the earlier observations reported are taken from experiments in which this key was used. Ultimately on account of objections to the length of time of charging, as well as to secure greater uniformity in the separate periods allotted to each part of the process, a new key was constructed, which proved very satisfactory in use, and which has been employed exclusively since that time. It consisted of a heavy $\frac{3}{4}$-second pendulum furnished with adjustable catches, by whose use it could be made to execute a single vibration through any required amplitude, and could be held suspended at the end of its swing.

The pendulum carried on its under side two insulated metal pieces, from each of which depended three small platinum wires.

These wires in the course of their vibration cut through drops of mercury connected with the poles of the battery, the poles of the condensers, the binding-screws of the galvanometer, and each other, in such a manner as to produce the desired connections.

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The amplitude of the vibration was fixed to give about one tenth of a second to the charging, one tenth of a second between the charge and discharge, and one tenth of a second to the discharge into each other, at last leaving the condenser plates in communication through the galvanometer.

The proper insulation of the wires at the key gave some trouble, but was at last secured by imbedding the wires in paraffine at all points of contact with the key, and placing the drops of mercury at the bottom of deep grooves in a paraffine block, separating those in the same groove from each other by a transverse groove of greater depth. In fairly dry weather, this arrangement gave satisfactory results. This key could be used to charge and discharge a single condenser; in fact, in the later experiments it was found better to use but one condenser, regulating its size to make the deflections manageable.

With the apparatus thus arranged and tested for connections and insulation, the labor of experiment was comparatively light. The condensers were charged and discharged several times, the electro-magnet meanwhile being inactive. The dynamo was then set in motion, the magnet excited, and the condensers charged and discharged as before. Usually this process was repeated several times before making any change in the apparatus, as will be seen in the tables which follow. Repeated tests were made to determine whether the dynamo or the electro-magnet by their direct action would affect the scale reading, but no motion of the index line could be detected when the machine was started and stopped by an assistant. This test was repeated, with the battery, condenser, and galvanometer circuits joined, in every combination assumed by them in the course of the experiment.

The magnet circuit was always closed. The charging battery was disconnected from the condensers $\frac{2}{10}$ of a second before the condensers were put upon the galvanometer.

In these experiments no attempt has been made to obtain accurate quantitative results, and as no care was taken to adjust the galvanometer to the same degree of sensitiveness, the readings in different series of experiments are not comparable.

The directive power of the earth upon the needle was very nearly neutralized by magnets placed near it, so that the torsion of the suspending fibre, which is constantly changing both as to direction and amount, comes to have a larger influence than is desirable upon the results. It is fortunate that the influence of a progressive change of this sort may be largely eliminated by a suitable order of experimentation.

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Several tables follow, containing results which seem to warrant the statements with which the paper commences.

In these tables, column *A* gives the number of the experiment in the series. *B* contains the observed galvanometer deflections when the magnet was inactive; *C*, deflections when the magnet was excited. *D* and *E* contain averages of the groups given in *B* and *C*. At the foot of the table is given the general average, and the deduced percentage variation.

Table I. Magnetic force perpendicular to the plates of the condenser. Two condensers used, each consisting of 11 disks of copper 8 cm. in diameter, with plates of mica between them. In this series the condenser which had the greatest normal capacity was placed between the poles of the magnet. An increase in the differential deflection of the needle when the magnet was excited indicates an increase of capacity in this condenser.

TABLE I.

A.	*B.*	*C.*	*D.*	*E.*
1	18			
2	19			
3	18			
4	18	....	18¼	
5	....	22		
6	....	22		
7	....	22		
8	....	20		
9	....	22		
10	....	20		
11	....	22		
12	....	20	....	21
13	18			
14	18			
15	18			
16	19	....	18½	
17	....	22		
18	....	20		
19	....	22		
20	....	20	....	21

TABLE II.

A.	*B.*	*C.*	*D.*	*E.*
1	30			
2	31	....	30½	
3	....	28		
4	....	28	....	28
5	33			
6	32	....	32½	
7	....	28		
8	....	28	....	28
9	35			
10	34	....	34½	

Table II. Exchanged the places of the condensers used in Table I., the smaller of the two being now placed between the poles of the magnet. Direction of the magnetic force as in Table I. In this series a diminished differential deflection of the needle with the excitement of the magnet shows an increase of capacity in the condenser between the poles.

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In Series I. and II. the distance between the poles of the magnet was not observed. These distances probably were not the same, for the pole pieces were removed in changing condensers.

Tables III. and IV. Magnetic force perpendicular to the plates of the single condenser. This was made of two disks of copper eight

TABLE III.

A.	*B.*	*C.*	*D.*	*E.*
1	47			
2	48			
3	47			
4	47	....	47.2	
3	....	46		
4	....	49		
5	....	47½		
6	....	49½		
7	....	48½	....	48.1
8	49			
9	—			
10	47			
11	45½			
12	—			
13	46	....	46.9	
14	....	49		
15	....	51		
16	....	49		
17	....	51		50
18	50			
19	49			
20	51	....	50	
21	....	53		
22	....	53	....	53
24	51½			
25	52	....	51.7	
26	....	55		
27	....	56	....	55.5
28	52½			
29	53	....	52.7	
Average . . .			49.7	51.6

Increase of capacity, 3¾ per cent.

TABLE IV.

A.	*B.*	*C.*	*D.*	*E.*
1	51			
2	54			
3	54			
4	54	....	53.2	
5	....	56		
6	....	56		
7	....	56	....	56
8	54			
9	54	....	54	
10	....	55		
11	....	55		
12	....	55½	....	55.1
13	53½			
14	53½	....	53	
Average . . .			53.4	55.5

Increase of capacity, 3½ per cent.

centimeters in diameter, with a sheet of mica between them. Between the two series of experiments the direction of the magnetic force was reversed. An increase of capacity equal to 3½ per cent is shown in both tables. Hence we conclude that the change in capacity is not reversed in sign with the reversal of the direction of the magnetic force.

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Tables V., VI., and VII. show the variation of this effect with the intensity of the field. In Table V. the poles were 1 mm. apart; in Table VI., $2\frac{3}{4}$ mm.; in Table VII., $4\frac{1}{2}$ mm. distant from each other.

TABLE V.

A.	*B.*	*C.*	*D.*	*E.*
1	167			
2	166	....	166.5	
3	....	197		
4	....	202	....	199.5
5	175			
6	175	....	175	
Average . . .			170.7	199.5
Increase of capacity, 17 per cent.				

TABLE VI.

A.	*B.*	*C.*	*D.*	*E.*
1	196			
2	193	....	194.5	
3	....	217		
4	....	218	....	217.5
5	190			
6	196	....	193	
Average . . .			193.7	217.5
Increase of capacity, 12 per cent.				

TABLE VII.

A.	*B.*	*C.*	*D.*	*E.*
1	177			
2	185	....	181	
3	....	194	....	192
4	....	190		
5	191	....	191	
6	....	197		
7	....	203	....	200
8	193			
9	185	....	189	
Average			187	196
Increase of capacity, 5 per cent.				

The single condenser used was made of four sheets of tinfoil 6 cm. by 6 cm., with paraffined paper between them. The direction of the magnetic force as in the preceding tables. The capacity was increased in each series; in Table V. about 17 per cent, in Table VI. 12 per cent, and 6 per cent in Table VII.

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Tables VIII. and IX. show results obtained by using a single condenser, whose plates were parallel to the lines of magnetic force. The condenser was made of forty copper strips, 6 mm. wide and 6 cm. long,

TABLE VIII.

A.	*B.*	*C.*	*D.*	*E.*
1	32			
2	32	....	32	
3	....	30		
4	....	$27\frac{1}{2}$	....	28.8
5	33			
6	33	....	33	
7	....	32		
8	....	33	....	32.5
9	32			
10	28			
11	33			
12	37			
13	34	....	34.7	
14	....	37		
15	....	35		
16	....	33	....	35
17	38			
18	38	....	38	
19	....	37		
20	....	35		
21	....	36	....	36
22	$38\frac{1}{2}$			
29	$37\frac{1}{2}$			
30	$37\frac{1}{2}$	....	37.8	
31	....	$37\frac{1}{2}$		
32	....	35		
33	....	$37\frac{1}{2}$	....	36.6
34	$38\frac{1}{2}$	....	38.5	
Average . . .			35.7	33.8
Decrease in capacity, 5 per cent.				

TABLE IX.

A.	*B.*	*C.*	*D.*	*E.*
1	71			
2	70			
3	69			
4	67	....	69.2	
5	....	65		
6	....	66		
7	....	68		
8	....	68	....	66.7
9	72			
10	73			
11	71			
12	74	....	72.2	
Average . . .			70.7	66.7
Decrease in capacity, 5 per cent.				

insulated by paraffined paper. The poles of the magnet were 10 mm. apart. In both of these tables the establishment of a magnetic field is seen to produce a diminution in the capacity of the condenser of about 5 per cent.

A series of experiments (see Table X.) made with a mica condenser, placed in the field with its plates perpendicular to the lines of magnetic force and with the poles 10 mm. apart, showed that its capacity was increased by about 5 per cent.

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TABLE X.

A.	*B.*	*C.*	*D.*	*E.*
1	83			
2	80	....	81	
3	....	88		
4	....	93	....	90
5	91			
6	90	....	91	
7	....	96		
8	....	97	....	96
9	93			
10	92	....	92	
11	....	100		
12	....	100	....	100
13	98			
14	92	....	95	
Average . . .			90	95
Increase of capacity, 5+ per cent.				

It is very difficult in such an investigation to prove the absence of error. It would also seem to be nearly as difficult to imagine a source of error which should reverse its sign, as in Tables III. and IV., when two condensers change places, and yet give consistent results showing an increase of capacity in both cases, — which should also show a change of sign when we pass from the use of condensers whose plates are perpendicular to the lines of force to those whose plates are parallel to those lines, — and, finally, which should change in amount with the intensity of the field.

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VIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A THERMOCHEMICAL ANALYSIS OF THE REACTION BETWEEN ALUM AND POTASSIUM HYDRATE.

By A. V. E. Young.

Communicated by the Corresponding Secretary, June 10, 1885.

PART I.

In the course of a thermochemical study of potassic aluminate I desired to use as one element of calculation the amount of heat evolved in the following reaction,

$$Al_2(SO_4)_3 . K_2SO_4 + 6\ KOH = 4\ K_2SO_4 + Al_2(OH)_6,$$

assuming in accordance with Thomsen's statement that the alum is equivalent, for this purpose at least, to aluminic sulphate. This quantity is given by Thomsen* as 30528 calories. He determines it directly by precipitation with potassic hydrate in the calorimeter, and, as a control, determines the heat of precipitation with three molecules of baric hydrate. The results of the two methods agree fairly well. This value is made by the same author the basis for the indirect determination of the formation heat of the chloride and several other compounds of aluminum, and this, notwithstanding the fact that he notes the complete precipitation of the aluminic oxide by five molecules of potassic hydrate instead of six, which would appear to indicate the formation of a basic precipitate. He evidently assumes that the addition of six molecules of the hydrate leaves the precipitate free of sulphuric acid, and that the agreement with the result obtained when baric hydrate is used affords confirmation of the assumption. Indeed, in other instances, e. g. sulphates of copper, cobalt, and cadmium, when the two methods do not give concordant results, he adopts the result by baric hydrate, and rejects that by potassic hydrate as being untrustworthy by reason of the formation of a basic precipitate. It would seem unsafe to assume, without experimental verification, that baric

* See Thermochemische Untersuchungen, i. 366.

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hydrate may not produce a basic precipitate as well as potassic hydrate, and thus render both methods open to the same objection.

However this may be, the results which I obtained soon led to the suspicion that the reaction with potassic hydrate was not so simple as is indicated by the above equation. One question after another arising which I was unable to answer, I have been led step by step to what may be called a thermochemical analysis of the reaction in question. The first part of the results obtained constitutes the substance of the following paper. At a later date, I hope to publish a determination of the precipitation heat of aluminic hydrate by a method free from these objections. The first series of experiments involves the determination of the reaction heat of alum and potassic hydrate, the proportion of the latter present varying from .5 to 10 molecules. This is followed by a parallel series determining the composition of the precipitates obtained in the calorimetric experiments. Before considering in detail the results of the first series, I give a brief description of the calorimetric methods and of the calculations that were used.

Method and Calculations.

The general method of heat measurement is that described by Berthelot. The calorimeter used was made after the specifications given by him* without essential variation. The inner platinum calorimeter has a capacity of somewhat more than 1,200 c.c. The stirrer is a simple one, a piece of platinum foil fused to a glass rod. The thermometers were made by Baudin of Paris especially for thermochemical work after specifications by Berthelot,† and were calibrated by Pernet at the Bureau International des Poids et Mesures. The zero points have been recently redetermined. The three pairs of duplicates taken together give a range of temperature from 0° to 33° C. They are graduated to fiftieths of a degree, and the readings were made, usually with the aid of a small hand lens, to $\frac{1}{200}$ of a degree, and often to $\frac{1}{400}$. The experiments were performed in a large basement room without artificial heat, where, during a portion of the year at least, the temperature conditions were fairly satisfactory. The operation consisted, with but one or two exceptions, in mixing in the calorimeter two portions of liquid of 500 c.c. For this measurement two flasks were used, their graduation being verified by weight.

Solutions containing the requisite quantity of constituents were prepared, diluted to somewhat less than 500 c.c., and allowed to stand in

* Essai de Mécanique Chimique, i. 140. † Ibid., p. 164.

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closed flasks beside the calorimeter until the following day, or perhaps during a longer interval. When ready for the calorimetric determination one of the prepared solutions was transferred with rinsing to the measuring-flask, (care being taken not to change unduly its temperature in the handling,) and filled to 500 c.c. with distilled water that had stood a day or longer on the same table. It was then poured into the calorimeter and its temperature taken, after thorough stirring, at intervals of five minutes. The change of temperature during this interval should not be more than .02°. At the same time, the second solution having been transferred to the second measuring-flask, its temperature in the flask was taken by a second thermometer in similar manner. Its change likewise should not be more than .02° per interval of five minutes; and it is also important that it should be close to that of the room, which was read from an ordinary thermometer.

When the temperature conditions were satisfactory, and the readings duly recorded, the contents of the second flask were poured as quickly as possible into the calorimeter, the mixture thoroughly stirred, and the resultant temperature recorded. The interval between the last reading of the initial temperatures and the first of the resultant temperature was in this series of experiments one and a half or two minutes, and with few exceptions the maximum temperature was reached in this time. Readings were then taken, always with stirring, every minute for about five minutes, and then at an interval of five minutes, in order to have a record of the rate of cooling.

There seems to be one unsatisfactory point in this method of manipulation; namely, the difficulty of obtaining the true temperature of the second volume of liquid while it still remains in the flask, and of transferring it to the calorimeter without consequent change. Experience will convince one of this difficulty in experiments where a variation of .01° is of considerable importance. My habit is to close the flask and shake it as thoroughly as possible before inserting the thermometer, and to see that its temperature at the time shall be such that it need not be left more than five or ten minutes before transferring to the calorimeter. Meantime the flask stands in a loose bag of flannel, supported by a frame that serves as handle so that the hand itself is distant several inches from the flask. Nevertheless, I have not infrequently obtained apparently accidental results, which varied from the mean notably more than the average variation, and of which the difficulty just described seems the probable cause. I hope later on to reduce, if not to eliminate, this uncertainty by a simple modification of apparatus.

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Calculations. — The unit of heat employed, the calorie, is the quantity required to raise one kilogramme of water one degree at the temperature of the experiment. The mean temperature after mixing is calculated by the following formula:

$$T_m = \frac{(A + d)\, T_a + B\,(T_b - t)}{A + d + B};$$

in which

T_m = mean temperature.
A = water equivalent in grammes of solution A in calorimeter.
d = water equivalent in grammes of calorimeter, stirrer, and thermometer.
B = water equivalent in grammes of solution B.
T_a = observed initial temperature of solution A in calorimeter.
T_b = observed initial temperature of solution B in flask.
t = correction in degrees to make the reading of the two thermometers correspond.

The temperatures T_a and T_b, recorded in the tables, are those actually observed. In the calculation of T_m the correction d is used, but no correction is made for difference between the observed zero and the actual zero, as it would not affect the final result. The temperature recorded as T_c is the difference between the calculated mean temperature and the resultant temperature; in other words, the change of temperature due to the reaction, and is positive unless otherwise specified.

The column f in the tables gives the factor by which T_c is multiplied to reduce the heat disturbance of the reaction in calories to molecular proportions, and H is this final result. The factor f is obtained as follows:

$$f = (A + B + d) \times \frac{\text{mol. wt.}}{\text{grms. taken}} \text{ (of alum)}.$$

In all the experiments of this paper the water equivalent of the calorimeter and its belongings is 8.5 grm., while A and B are the volumes in cubic centimeters of the constituent solutions reckoned as grammes of water (Berthelot's method of calculation*), each numerically equal to 500 c.c. unless otherwise specified. $t = .008°$.

Limit of Error. — The reading of temperature is by far the most considerable element limiting the certainty of experimental observation. The quantity of alum used, 20.667 grm., is weighed to one

* Essai de Mécanique Chimique, i. 190.

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part in more than twenty thousand. The KOH solution is titrated against oxalic acid, and its titration confirmed gravimetrically. The quantity used in an experiment varied from 10.67 c.c. to over 200 c.c. This was measured in a burette to .05 c.c., which would make the maximum variation considerably less than one per cent of the quantity measured, even when the latter was at its minimum. Whereas, if we put the limit of temperature reading at .005°, and consider that the change in temperature depends upon three separate readings, the maximum of error should be .01°, or .005° putting the limit of reading at .0025°. This would be a very large per-cent variation in many of the experiments when the quantity measured falls considerably below 1°. Inspection of the tabulated data will show that in many cases the observed variation of T_c is much smaller than the calculated maximum; e. g. the first six experiments of Table I., where it is only .001°. In most of the experiments a variation of .005° in T_c makes a variation of .24 Cal. in H.

Series I.

The numerical data of these experiments are recorded in Table I. The alum used was the commercial article, well crystallized and free of iron. Of it 20.067 grm. were used in each experiment, and the solution prepared as already described. The proportion of water was about 2,600 molecules to one of alum; in Thomsen's experiments, 2,400. In column h is recorded the rate of heat disturbance per molecule of KOH. The results H and h are seen graphically expressed in Plate I., where x is the number of molecules of KOH added, and y in Line I. represents H, in Line III., $h \times 10$.

Inspection of Line I. shows that the heat evolution increases with the quantity of KOH, reaching a maximum at $x = 6$ or 6.5, and from this point diminishes until $x = 10$, when the re-solution of the precipitate in the excess of KOH is complete. This means that the solution of the precipitate in excess of KOH is accompanied by heat absorption, or is endothermic. It will be shown farther on that the addition of KOH beyond $x = 8.5$ causes no further heat disturbance, and that 8.13 mol. KOH completely redissolve the precipitate; hence, in constructing the line, the value of y at $x = 8.13$ is made the same as at $x = 10$.

Line III. reveals still more. It shows a constant rate of heat evolution per molecule of KOH from $x = .5$ to $x = 1$. At this point it drops abruptly. Now in the analytical part it will be shown (see Plate II. Line V.) that precipitation begins between $x = 1$ and

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$x = 1.5$, probably at $x = 1.13$. Hence, in constructing Line III. the minimum is put hypothetically at $x = 1.13$, instead of at $x = 1.5$ which is the point actually determined. Inasmuch as the precipitate at first produced redissolves in excess of alum up to $x = 1.13$, the drop in the line at this point indicates probably that this re-solution also is accompanied by heat absorption. This will be evident upon considering that the heat disturbance, h, is a positive resultant, made up of both positive and negative elements. The principal positive element is the formation heat of potassic sulphate, and since this in all probability remains approximately constant for equal portions of KOH entering into combination, it follows that the negative element increases at the point $x = 1.13$ in consequence of precipitation. In other words, precipitation is accompanied by heat evolution, and re-solution of the precipitate by heat absorption.*

Beyond $x = 1.13$ there is evidently a tendency to rise slightly up to $x = 5$, or thereabouts. The break at $x = 4.8$ is within the limit of error, since the larger value recorded in Table I. gives the alternative point, $x = 4.8$, just above the line as seen in the plate. Indeed, the increase between $x = 1.13$ and $x = 5$ depends upon differences which lie so close to the limit of experimental error that one must hesitate to consider it more than probable. It would be interesting to establish it beyond doubt, in view of the analytical results shown in Plate II., Line VII. There can be no doubt, however, that the line drops beyond $x = 5.12$, as would be expected.

It is to be noted that the maximum in Line I. occurs at $x = 6$ or 6.5; while in Line III. it occurs at $x = 5$, which is the point at which the aluminic oxide is completely precipitated. This leads to the question, What causes the continued heat evolution after the precipitation is total? the discussion of which must be deferred until the analytical results have been described. The three experiments recorded in Table III. serve, however, to fix one point bearing thereon. 4.8 mol. KOH were added to one of alum in the usual conditions. Then to this mixture were added in the calorimeter the remaining 1.2 mol. KOH, in the proportionate quantity of water, and the heat evolution measured. The results are fairly satisfactory, considering that the necessary conditions of the experiments were not the best for calorimetric measurement. They serve to show, at least, that the continued evolution of heat between $x = 4.8$ and $x = 6$, in Series I., may be accounted for by the action of the 1.2 mol. KOH on the

* See similar case of lead, Thomsen, i. 377.

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precipitate formed by the 4.8 mol. A previous experiment, made by adding KOH in the calorimeter to the liquid portion of the mixture 1 alum + 5 KOH (the precipitate being removed), gave zero for a result.

Series II.

In the second series of experiments the same quantity of alum was dissolved, 10 mol. KOH added, and the whole made up to 500 c.c., as in Series I. To this was added in the calorimeter 500 c c. of sulphuric acid solution, containing of H_2SO_4 quantities varying from .5 to 3 molecules. The numerical data are recorded in Table II. It will be seen that the rate of heat disturbance per molecule of H_2SO_4 is practically constant for $n = .5$ and $n = .75$, but increases at $n = 1$; the first precipitation by neutralization of KOH occurs between $n = .75$ and $n = 1$. The rate then increases to $n = 2.2$, when it again drops. Instead of expressing these direct results graphically, I have calculated from them (at least from Exp. 42–48) the corresponding points in the Lines I. and III. The possibility of this calculation will be apparent from considering that H in Series II. is the formation heat of potassic sulphate plus or minus the heat disturbance involved in separating the equivalent potassic hydrate from whatever form of combination it may be in before the addition of sulphuric acid. If we assume that the n mol. H_2SO_4 (from $n = 1.5$ to $n = 2.2$) are converted into K_2SO_4, and count the formation heat of the latter as a known quantity, we have the means of calculating indirectly the values of y in Series I. for $x = 6$, 7, and 10. These values locate the supplementary Lines II. and IV., Plate I. They are separated by a small and approximately constant quantity from the Lines I. and III.

A similar discussion of the values for $n = .5$ and .75 will make evident whether or not the addition of KOH beyond 8.13 mol. has any effect. The formation heat of K_2SO_4 is according to Thomsen 31.288 Cal. One half of this, 15.644 Cal., is larger by .96 than the mean result of Exp. 36–39, Series II., which would indicate that heat was absorbed in liberating KOH from its previous state of combination, and hence that the combination of the 9th and 10th mol. in Series I. was accompanied by heat evolution. This, if true, would be an interesting fact; but the question arises, May not the formation heat of K_2SO_4 in Exp. 36–39 be less than 31.288 Cal., this value having been determined for a degree of concentration six times as great? I therefore determined it independently, using, first, the same quantities of KOH and H_2SO_4 as occur in the reaction $n = .5$, and

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then six times their quantities, the volume 1,000 c.c. remaining the same throughout. In the last case, the proportion is about the same as in Thomsen's experiment. The data are shown in Table IV. At the degree of concentration which corresponds to Exp. 36–39, the formation heat of $\frac{1}{2}$ K_2SO_4 is found to be (Exp. 57–61) 14.63 Cal., which agrees with H in Exp. 36–39; while for one sixth this dilution H is found to be 31.26 or 15.63 for $\frac{1}{2}$ K_2SO_4; Exps. 53, 54, correspond to Thomsen's conditions.

This proves that the second half of the 9th mol. and the 10th mol. in Series I. are not in chemical combination, or, at least, that there is no evidence of it in the thermal phenomena. In other words, the heat disturbance ceases when 8.13 mol. KOH have been added, as indicated in Line I., Plate I.

As dilution was found to affect the determination of the formation heat of K_2SO_4, it became desirable to test its influence upon the resultant H of Series I., in which this formation heat is the principal element. To do this the reaction heat of 6 mol. KOH on 1 of alum was determined, the absolute amount of substance undergoing change in the standard volume, 1,000 c.c., being only one fourth the quantity used in Exp. 23–26, Series I. These data are recorded in Table V. The mean result of the five experiments is 29.26 Cal., in place of 30.66 by the previous experiments.

It seems not improbable, in view of these facts, that the tendency of the Line III., Plate I., to rise between $x = 1.5$ and $x = 5.1$, may be due to the increase in the amount of substance undergoing change in the unit of volume.

The complexity of the thermochemical results thus far described made evident the necessity of a sharper definition of the chemical changes actually taking place in the calorimeter. The study of these constitutes the second part of this paper.

PART II.

General Method. — It would seem that the most direct method of obtaining evidence as to the exact chemical change would be to determine the composition of the various precipitates produced in the calorimetric experiments. The impossibility, however, of washing them without changing their composition, indicated rather the analysis of the filtrate from them as the preferable method. Either one determines only the total change in the distribution of constituents between the soluble and insoluble portions of the system.

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The method pursued was the following: 50 c.c. of alum solution, containing five grammes of the crystallized salt, were made up to a little less than 125 c.c. The required quantity of KOH solution was also made up to about the same volume. These two solutions were then thoroughly mixed, the volume of the mixture made up accurately to 250 c.c. (T 20° C.), again well shaken, and thrown upon a dry filter, the filtration being hastened in some instances by using the pump. From the filtrate separate portions of 50 c.c. each were taken, in which were made duplicate determinations of SO_3 and Al_2O_3, and in several instances of K_2O. The SO_3 was determined, of course, by precipitation with $BaCl_2$; the Al_2O_3, by precipitation with NH_3; and the K_2O was weighed as sulphate after the removal of Al_2O_3. The proportion of constituents and water is the same as in the calorimetric experiments, the scale being simply reduced to one fourth.

Analyses somewhat similar have been made by S. U. Pickering* of the precipitates obtained from aluminic sulphate by addition of varying quantities of Na_2CO_3. His method was to determine the SO_3 and Al_2O_3 in the precipitate itself after thorough washing, although he recognized the fact that its composition was changed by the operation. This would be a serious objection to the use of this method for the purposes of this investigation, although less so in his experiments undertaken from a different standpoint. Our results, so far as they cover the same points, do not conflict in the general direction of their indications, although quantitatively they differ somewhat.

Mills also has determined simply the amount of Al_2O_3 precipitated from alum solution by varying quantities of Na_2CO_3.†

It should be noted that the method of this investigation gives no evidence as to the degree of hydration of the precipitate; that point I am obliged to pass by.

In the first experiment of this series (Exp. A) the method was applied in blank to a solution of alum, no KOH being added. The results obtained were:

Al_2O_3 = .1080 grm.	SO_3 = .3321 grm.
= .1074	= .3326
Mean = .1077	Mean = .3324

As these correspond to 1 grm. alum taken, multiplying by 100 converts them into per cents. Correcting for the volume of pipettes and

* Chemical News, xlv. 121, 133, 146.

† Journal of Chem. Society, [2,] xli. 341.

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flask makes them respectively 10.90 and 33.64. Adding to these the determinations of K_2O and H_2O, made by separate experiments, makes the complete analysis of the alum used as follows:

	Found.	Cal.
Al_2O_3	10.90	10.76
SO_3	33.64	33.75
K_2O	9.94	9.93
H_2O	45.64	45.56
	100.12	100.00

It is evident that the difference between the results of A and of corresponding results of subsequent experiments in which precipitation does occur, gives the amount of Al_2O_3 and SO_3 in the precipitate. The final results of each experiment are reckoned as parts of Al_2O_3 in 100 parts of anhydrous precipitate, and as parts of Al_2O_3 precipitated out of 100 parts of Al_2O_3 present in the total system. The following is an example of a calculation in full: —

	Al_2O_3.	SO_3.
A =	.10766 grm.	.33231
D =	.0689	.31134
Precipitate =	.03876	.02097

$$\text{Anhydrous precipitate} = \frac{.03876 \times 100}{.03876 + .02097} = 64.89\%\ Al_2O_3.$$

$$Al_2O_3 \text{ of precipitate} = \frac{.03876 \times 100}{.10766} = 36.00\% \text{ of total } Al_2O_3.$$

The data of this series of experiments are recorded in Table VI. The quantity of KOH varies, as will be seen, from 1.5 to 8 molecules.

Before discussing the results, I describe another series made to reverse, as it were, the conditions of the former.

Fifty c.c. of alum solution were taken as before, and to this ten molecules KOH added, and the whole made up to a little less than 125 c.c. Sulphuric acid solution, containing quantities of H_2SO_4 proportional to 1.5, 2, 2.5, and 4 molecules, was added, and the mixture brought accurately to 250 c.c. (T 20°), thoroughly shaken, filtered, and the filtrate analyzed as usual. The only variation was in Exp. T, when 5 mol. HCl were used in place of 2.5 H_2SO_4, and this will be more particularly discussed in a subsequent publication. The data of these experiments are recorded in Table VII.

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The calculation of the composition of the precipitate is similar to that in the preceding series, except that account must be taken of the SO_3 added.

In three experiments, viz. *H*, *T*, and *S'''* (in *H* and *T* the total amount of precipitate was at its maximum), the K_2O in the filtrate was determined. The full calculated amount being found, it was deemed unnecessary to determine it at other points, since it evidently formed no part of the precipitate.

Discussion. — The results of the first two series are graphically expressed in Lines V., VI., VII., and VIII., Plate II. In Line V., $x =$ number of molecules of KOH added, and $y =$ per cent of total Al_2O_3 found in the precipitate. While in Line VII., $x =$ the same, but $y =$ parts of Al_2O_3 in 100 parts of anhydrous precipitate. Continuing Line V. beyond $x = 1.5$ and $x = 8$ toward the axis of x indicates $x = 1.13$ and $x = 8.13$ as the probable points respectively of initial and final precipitation. The line reaches its maximum at $x = 4.8$, making the precipitation of the Al_2O_3 complete at this point.

Line VII. shows that the first precipitate is the least basic, containing only 64% of Al_2O_3; that from $x = 1.5$ to $x = 4$ there is apparently a slight increase of basicity, but that from $x = 4$ to $x = 4.8$ the increase is more rapid; that between $x = 4.8$ and $x = 6$ the rapidity of change is still greater; that at $x = 6$ it drops back again, leaving a precipitate free of SO_3 at $x = 7$. It will be noticed that $x = 4.8$ and $x = 6$ are salient points in these lines, as they are in Lines I. and III., expressing the thermal phenomena.

The points in Line VI., $x = 5$, 6, and 7, are obtained from Exp. *N*, *O*, and *T*, by making x the number of molecules of KOH left unneutralized by the H_2SO_4 added. It will be seen that they approximate closely to the corresponding points in Line V., the difference being probably within the limits of experimental error. This evidently means that, when the same amount of free KOH is present, the same precipitate is obtained, whether it come from adding KOH to alum, or from neutralizing the excess of KOH in the alkaline solution of Al_2O_3 obtained by adding 10 KOH to alum. This result was unexpected, and suggested at once the possibility of a chemical equilibrium existing between the constituents of the soluble and of the insoluble portions of the system. To test this idea, Exp. *P* was made, using 4 mol. H_2SO_4. Assuming that 4 mol. KOH out of the ten added are uncombined with H_2SO_4, the 4 mol. H_2SO_4 now added would neutralize them, leaving an excess of 2 mol. H_2SO_4, and making a system, neglecting the K_2SO_4, constituted of 1 mol. Al_2O_3 and 2 H_2SO_4, the

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same which we suppose to exist when 2 mol. KOH are added to 1 mol. alum. Putting $x = 2$, therefore, the results of Exp. *P* give the points *P* in the Lines VI. and VIII., which approach at least the corresponding points in V. and VII. Regarding this as a further indication of an equilibrium, I varied the experiment in the following manner (Exp. *Q*): The usual 50 c.c. of alum solution were taken, 6 mol. KOH added, and the whole made up to 250 c.c. Another portion of 50 c.c. alum solution was then taken, and made up to nearly 250 c.c. The two solutions thus prepared were then mixed, made up to 500 c.c., thoroughly shaken, filtered, and portions of 50 c.c. taken from the filtrate for analysis, as usual. The total system here is evidently the same in the proportion of its constituents (water included) as would be obtained by mixing 1 mol. alum and 3 mol. KOH in a volume of 250 c.c. At the same time, we can calculate from Exp. *I*, Table VII., what would be the composition of the precipitate, assuming that it remained the same as produced by 6 mol. KOH in the first mixture, increased only by the remaining 9.47% of the total Al_2O_3 of the first portion; the KOH uncombined with H_2SO_4 in that portion taking SO_3 from the second portion of alum, but causing no increase of precipitate since it is equivalent to only about .14 mol. KOH. The precipitate thus calculated would contain 50% of the total Al_2O_3 of the system, and have a composition of 95.29% Al_2O_3 to 4.71% of SO_3. This gives the crossed points *Q* ($x = 3$). But actual analysis of the filtrate gives for the precipitate the results recorded in *Q*, Table VIII., and the points *Q* in the Lines VI. and VIII. This shows that the initial distribution of constituents between the soluble and insoluble portions of the system has changed completely, approaching that obtained by adding to 1 mol. alum 3 mol. KOH. The change in this case consists only in an increase of SO_3 in the precipitate.

Another experiment was then made (Exp. *R*) by mixing in similar manner (1 alum + 6 KOH) in 250 c.c. and (1 alum + 1.5 KOH) in 250 c.c.; making a total system equivalent to 1 alum + 3.8 KOH in 250 c.c. Calculating as in *Q*, from Exp. *B* and *I*, the initial composition of this mixed precipitate, and on the assumption that the unneutralized .1 mol. KOH of the 6 mol. KOH is added to the 1.5 mol. in the second portion, we obtain the crossed points *R* ($x = 3.8$). Analysis of the filtrate, on the other hand, gives the points *R* ($x = 3.8$) in the Lines VI. and VIII., which likewise shows a very considerable change in the precipitate, and a close approach to the system obtained by adding 3.8 mol. KOH to 1 mol. alum. In this case the change

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is more complex than in Q, consisting in the precipitate acquiring both Al_2O_3 and SO_3. In other words, the equilibrium has moved the crossed point R up to the point R in VI., and the crossed point R down to R in VIII.

The results already described indicate unmistakably the existence of the equilibrium; but, to vary the evidence still more, Exp. S', S'', and S''' were made, as follows: —

Aluminum was dissolved in KOH solution and the KOH exactly neutralized by HCl, independent experiments having proved that the precipitate thus obtained is free of acid. The volume of this mixture having the freshly precipitated hydrate in suspension was brought up to 250 c.c. Fifty c.c. of alum solution (= 5 grm. alum) were then added, the whole made up to 500 c.c. and thoroughly mixed. Before filtering, portions of 50 c.c. each were withdrawn with a pipette, care being taken to insure the uniform distribution of the suspended precipitate by constant stirring. In these portions the precipitate was redissolved by HCl and the total Al_2O_3 of the system determined. The remainder of the mixture was filtered as usual, and portions of 50 c.c. of its filtrate taken for the usual determinations of SO_3 and Al_2O_3. The differences between the total Al_2O_3 and SO_3 and the Al_2O_3 and SO_3 found in the filtrate give the composition of the precipitate. In S' the amount of Al_2O_3 added as precipitate was 1.12 times that added as alum, making a proportion of 2.12 mol. Al_2O_3 to 3 mol. SO_3 in 500 c.c. of volume; equivalent to 1 Al_2O_3 and 1.4 SO_3 in approximately 250 c.c. This so far as relation between Al_2O_3 and SO_3 is concerned, should be equivalent to 1 alum + 3.2 KOH. Using therefore the analytical results of S', Table VIII., and making $x = 3.2$, we obtain the dotted points S', Plate II., approximating closely to the values otherwise obtained; whereas had the precipitate remained unchanged it would have been 100% Al_2O_3 and contained 52.82% of the total Al_2O_3. These values are represented by the crossed points S'. The change consists mainly in acquiring SO_3.

Exp. S'' is similar, the only variation being in the quantity of precipitated Al_2O_3 added. The results are shown in the points S'' ($x = 2.5$); whereas the crossed points S'' indicate what would have been the results had the precipitate remained unchanged. Here, too, the change is in acquiring SO_3.

Still another experiment, S''', was made, varying again the quantity of Al_2O_3 added. The actual results are shown in the points S''' ($x = 2$), and the initial precipitate in the crossed points, S'''. Here it is apparent that the change consists in gaining SO_3 and losing Al_2O_3.

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The proof of equilibrium is indubitable, the initial precipitate gaining or losing Al_2O_3 or SO_3 as may be necessary to bring about the characteristic distribution of constituents for the given conditions. It is also apparent that K_2SO_4 plays no part, and may be considered as practically outside the system, since its presence in quantity varying from less than one molecule to more than ten molecules has not disturbed the leading phenomenon.

Another fact may be noted here. The corresponding points in the Lines V., VI., VII., and VIII., that lie to the right of $x = 5$, approximate closely, probably within the limits of experimental error. To the left of $x = 5$, the divergence is greatest, but the difference in every instance lies on the side of approach to the Lines V. and VII. from the initial points, never going beyond. The probable explanation of this lies in the fact that, in all the experiments yielding the Lines V. and VII., also the points of the other lines to the right of $x = 5$, the system in its initial state is homogeneous. While in the remaining experiments, with the single exception of Exp. *P*, it is non-homogeneous (liquid and solid). It is not strange, then, that this non-homogeneity exercises a retarding influence upon the equilibrium. It is rather a matter of surprise that it should not prove more of an obstacle than it does.

Effect of Temperature, Time, and Dilution on the Equilibrium.

Temperature often exerts an influence in reactions such as we have been describing, and to test its effect in this instance is the object of the three following experiments, *E'*, *E''*, and *E'''*. In the first place two successive experiments were made as nearly alike as possible, in order to measure the probable variation in the final results of a single experiment. I give the details in full. The solutions were prepared in the usual manner, 4 mol. KOH being added to 1 mol. alum. The temperature of the room in both experiments was about 23° C., but the contents of flasks before bringing up to standard volume and before taking out portions of 50 c.c. were cooled, as in previous experiments, to 20°. The results were as follows: —

	E'.		*E''*.	
	Al_2O_3.	SO_3.	Al_2O_3.	SO_3.
Found in 50 c.c. I. =	.0174 grm.	.28221	.0159	.28203
II. =	.0174	.28210	.0162	.28190
Mean =	.0174	.28216	.0161	.28197

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	E'.		E''.	
	Al_2O_3.	SO_3.	Al_2O_3.	SO_3.
A =	.10766 grm.	.33231	.10766	.33231
E' =	.0174	.28216	.0161	.28197
Precipitate =	.09026	.05015	.09156	.05034

Anhydrous precipitate =	64.28% Al_2O_3	64.52% Al_2O_3
	= 35.72% SO_3	35.48% SO_3
Precipitate =	83.84% of total Al_2O_3	85.05% of total Al_2O_3

It will be seen that the SO_3 determinations do not differ appreciably more than the duplicate determinations of SO_3 in the same solution; while the amounts of Al_2O_3 obtained, differ by more than a milligramme, one part in seventeen. So in another instance, .2893 and .2899 grm. SO_3 were obtained in two experiments entirely distinct from the beginning. It would almost seem that the equilibrium were more sharply defined with reference to SO_3 than to Al_2O_3. Yet it should be borne in mind that the amounts of SO_3 actually weighed are always large, .28 grm. or more, while the amounts of Al_2O_3 weighed were as low as .01 grm., and hence the experimental determination of SO_3 is less affected by error than that of Al_2O_3.

The final results being dependent on the ratio between differences, small compared with the quantities actually measured, considerable latitude of variation must be allowed.

The experiment was then repeated, E''', the only variation being that, after the flask was filled to 250 c.c. (at 21°), it was heated to about 50–55° for twenty-five minutes, then turned into a large beaker with glass cover and heated fifteen minutes more, and finally boiled two or three minutes. The liquid on the cover was rinsed off with the solution, and the whole thrown while boiling hot upon a dry filter, which was covered during the ten minutes of filtration. The filtrate was then cooled to 20°, and portions of 50 c.c. taken as usual for analysis. The loss of water by evaporation could not have been great, and would not affect the ratio between Al_2O_3 and SO_3. The results were:

	Al_2O_3.	SO_3.
I. =	.0148	.30473
II. =	.0148	
Mean =	.0148	.30473

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This makes a precipitate containing 86.25% of the total Al_2O_3, with a composition of 77.10% Al_2O_3 and 22.90% SO_3. The precipitate at the temperature of boiling has, therefore, lost considerable SO_3, while the ratio of the Al_2O_3 precipitated to the total has not much changed.

Exp. E^{IV}. A second variation was made to test the influence of dilution on the equilibrium, since many of the experiments already described indicate that water plays a part in the reaction besides that of a mere solvent. Alum and KOH in the same quantity as in E', E'', and E''' were mixed, and the solution made up to 1,000 c.c., instead of 250, making the absolute quantity in unit of volume one fourth what it was in the preceding experiments. Of the filtrate, portions of 100 c.c. were taken, instead of 50, and the quantities of SO_3 and Al_2O_3 found were multiplied by two in order to make them comparable with the others. The results were:

	Al_2O_3.	SO_3.
I. =	.0162	.28570
II. =	.0160	.28578
Mean =	.0161	.28574

This indicates a precipitate containing 85.05% of total Al_2O_3, and of composition 66.29% Al_2O_3 and 33.71% SO_3.

Dilution also has tended to diminish SO_3 in the precipitate without changing the proportion of Al_2O_3 precipitated.

Is the equilibrium a function of time also? To answer this a mixture was prepared (Exp. E^{V}) at the same time as E', and in precisely the same manner. But instead of filtering at once as in E', the mixture was allowed to stand in a closed flask at the temperature of the room for seven days, and then filtered as in E', and the filtrate analyzed. The result was:

	Al_2O_3.	SO_3.
I. =	.0152	.28210
II. =	.0146	.28217
Mean =	.0149	.28214

This makes a precipitate containing 86.12% of the total Al_2O_3, and in composition 64.89% Al_2O_3 and 35.11% SO_3, or practically the same as in E'. Here, too, is to be seen the close agreement in quantity of SO_3 and the greater variation in Al_2O_3.

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This experiment was suggested by the fact that the basic filtrates obtained by adding one or more molecules of KOH, and removing the precipitate, yield a second precipitate on standing, the length of time apparently depending on the degree of basicity. This second precipitate is also produced in a few minutes by boiling or by adding a considerable quantity of water. Exp. E^{V} is therefore interesting as showing that time does not affect the equilibrium while the original precipitate remains in the system.

Conclusion.

It is clear, from the evidence herein set forth, that in the reaction which has been the subject of investigation we have another instance of chemical equilibrium or mass reaction, and the question at once arises, What is the cause of it? Without attempting to answer this definitely at present, we suggest the probability that it may be due to the progressive dissociation by water of basic compounds of Al_2O_3 and SO_3 on the one hand, and of potassic aluminate on the other. It would appear from Exp. S', S'', and S''', that $Al_2O_3 . 3\ SO_3$ must itself be partly dissociated in water solution, and it is not improbable that the matter may be still further complicated by the dissociation of another substance formed from the products of decomposition of the first. I hope to obtain definite evidence upon this point, by continuing a line of investigation already begun. That the basic sulphates of alumina are dissociated, is apparently indicated by the fact already cited, that the filtrates in experiments B to H yield a second precipitate on heating, diluting, or standing some length of time. While the crystallized potassic aluminate to which Fremy assigns the formula, $K_2O . Al_2O_3 . 3\ H_2O$, decomposes on the addition of water with the separation of aluminic hydrate.

However that may be, it is evident, (1.) that the reaction between alum and KOH is not by any means as represented in what may be called the ideal equation cited in the beginning of this paper, but that it is much complicated by secondary reactions which render it entirely unsuitable for the determination of the formation heat of the sulphate and other compounds of alumina, although the numerical error introduced by its use may not be great; and (2.) that these secondary reactions are of the nature of chemical equilibriums or mass reactions, the distribution of the constituents of the system about the line of solubility being a function of temperature, volume (i. e. dilution), and total mass of constituents.

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TABLE I.

1 Alum + n KOH.

$A = B = 500.$ $d = 8.5.$ $f = 47655.4.$

No. of Exp.	$n.$	$T_a.$	$T_b.$	$T_m.$	$T_c.$	$H = T_c \times f.$	$h = H \div n.$	Mean $H.$	Mean $h.$
		°	°	°	°	Cal.	Cal.	Cal.	Cal.
1	0.5	16.66	17.275	16.96	.060	2.86	5.72	2.85	5.69
2	0.5	16.4575	17.2225	16.833	.0595	2.84	5.67		
3	1.0	16.6675	17.2925	16.973	.1195	5.70	5.70	5.72	5.72
4	1.0	16.57	17.52	17.037	.1205	5.74	5.74		
5	1.5	16.70	17.0675	16.878	.1695	8.08	5.39	8.09	5.39
6	1.5	16.826	17.73	17.27	.1700	8.10	5.40		
7	2.5	17.02	18.073	17.538	.287	13.68	5.47	13.58	5.43
8	2.5	16.6075	17.04	16.818	.283	13.49	5.39		
9	2.5	16.545	17.40	16.965	.285	13.58	5.43		
10	4.5	17.08	17.93	17.497	.513	24.45	5.43	24.42	5.43
11	4.5	16.525	17.16	16.836	.514	24.50	5.44		
12	4.5	17.44	18.255	17.84	.510	24.31	5.40		
13	4.8	16.18	17.0525	16.609	.5335	25.42	5.30	25.79	5.37
14	4.8	17.2125	17.845	17.522	.548	26.12	5.44		
15	4.8	17.37	18.5775	17.965	.535	25.50	5.31		
16	4.8	16.4325	17.80	17.107	.548	26.12	5.44		
17	5.12	17.03	16.92	16.971	.594	28.31	5.53	28.39	5.55
18	5.12	17.06	17.68	17.363	.5945	28.33	5.53		
19	5.12	16.78	17.75	17.257	.5955	28.38	5.54		
20	5.12	16.17	17.0075	16.581	.599	28.55	5.58		
21	5.5	16.69	17.46	17.068	.632	30.12	5.48	30.14	5.48
22	5.5	16.49	17.35	16.912	.633	30.17	5.49		
23	6.0	19.5825	20.15	19.86	.640	30.49	5.08	30.66	5.11
24	6.0	19.84	20.5075	20.167	.633	30.17	5.03		
25	6.0	16.66	17.84	17.241	.6515	31.05	5.18		
26	6.0	16.6925	17.62	17.148	.6495	30.95	5.16		
27	6.5	16.2375	16.8825	16.553	.647	30.83	4.74	30.83	4.74
28	6.5	16.62	17.895	17.248	.6495	30.95	4.76		
29	6.5	16.445	17.705	17.066	.644	30.69	4.72		
30	7.0	19.15	19.72	19.429	.621	29.59	4.23	29.59	4.23
31	10.0	16.9725	18.01	17.483	.617	29.40	2.94	29.27	2.93
32	10.0	16.46	17.84	17.14	.610	29.07	2.91		
33	10.0	16.62	17.74	17.171	.619	29.50	2.95		
34	10.0	19.26	20.34	19.791	.6115	29.14	2.91		
35	10.0	19.1975	20.21	19.696	....	29.22	2.92		

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TABLE II.

(1 Alum + 10 KOH) + n H_2SO_4.

$A = B = 500.$ $d = 8.5.$ $f = 47655.4.$

No. of Exp.	n.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times f$.	$h = H \div n$.	Mean H.	Mean h.
		°	°	°	°	Cal.	Cal.	Cal.	Cal.
36	.50	19.2575	20.49	19.865	.305	14.54	29.07	14.68	29.36
37	.50	19.41	20.445	19.919	.311	14.82	29.64		
38	.75	17.81	19.14	18.465	.4575	21.80	29.07	21.83	29.10
39	.75	17.8175	19.0075	18.404	.4585	21.85	29.13		
40	1.00	18.19	19.5525	18.862	.628	29.93	29.93	30.05	30.05
41	1.00	18.21	19.725	18.957	.633	30.17	30.17		
42	1.50	17.92	18.305	18.107	.998	47.56	31.71	47.39	31.60
43	1.50	17.9675	18.9375	18.444	.991	47.23	31.49		
44	2.00	17.8975	18.98	18.43	1.340	63.86	31.93	63.55	31.77
45	2.00	19.094	19.65	19.366	1.3415	63.93	31.97		
46	2.00	17.605	19.0375	18.311	1.319	62.86	31.43		
47	2.20	17.82	19.0575	18.43	1.4575	69.46	31.57	69.28	31.49
48	2.20	18.22	18.53	18.37	1.450	69.10	31.41		
49	3.00	17.80	18.665	18.225	1.785	85.07	28.36	85.07	28.36

TABLE III.

(1 Alum + 4.8 KOH) + 1.2 KOH.

$A + d = 1008.5.$ $B = 124.96.$ $f = 47655.4.$

No. of Exp.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times f$.	Mean H.
	°	°	°	°	Cal.	Cal.
50	18.08	18.67	18.144	.086	4.10	3.83
51	17.57	17.87	17.602	.073	3.48	
52	17.0475	16.565	16.993	.082	3.91	

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TABLE IV.

$2\,KOH + H_2SO_4$. $A = B = 500$. $d = 8.5$.

No. of Exp.	n = grm. of H_2SO_4.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times \frac{1008.5 \times 98}{n = \text{grm. } H_2SO_4}$	Mean H.
		°	°	°	°	Cal.	Cal.
53	6.8071	17.6925	18.45	18.064	2.1435	31.12	31.26
54	6.8071	17.64	18.9075	18.264	2.1385	31.05	
55	6.227	14.62	15.43	15.018	1.9895	31.58	
56	6.227	15.27	15.96	15.608	1.972	31.30	
57	1.0391	17.1725	19.1275	18.138	.812	29.43	29.26
58	1.0391	18.30	19.45	18.863	.3065	28.91	
59	1.024	14.1675	14.8950	14.524	.311	29.76	
60	1.024	14.845	15.485	15.158	.307	29.38	
61	1.024	14.31	15.6275	14.959	.301	28.81	

TABLE V.

1 Alum + 6 KOH. $A = B = 500$. $d = 8.5$.

No. of Exp.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times \frac{1008.5 \times 948.24}{5}$	Mean H.
	°	°	°	°	Cal.	Cal.
62	18.76	19.83	19.287	.1505	28.82	29.26
63	19.01	20.07	19.532	.148	28.34	
64	19.13	19.77	19.443	.157	30.06	
65	19.54	19.9075	19.718	.152	29.10	
66	19.9925	20.22	20.101	.1565	29.96	

TABLE VI. — Analyses.

1 Alum + x KOH.

Exp.	x.	Grm. Al_2O_3 found in 50c.c. of Filtrate.	Grm. SO_3 found in 50c.c. of Filtrate.	Al_2O_3 in 100 pts. of Prec.	SO_3 in 100 pts. of Prec.	K_2O in 100 pts. of Prec.	Per cent of total Al_2O_3 in Prec.
A	0.	.10766	.33231	0.	0.	0.	0.
B	1.5	.09738	.32651	63.93	36.07	....	9.55
C	2.0	.08310	.31883	64.56	35.44	....	22.81
D	2.5	.0689	.31134	64.89	35.11	....	36.00
E	4.0	.01995	.28588	65.39	34.61	....	81.47
H	4.79	.0	.28967	71.63	28.37	0.	100.
I	6.0	.0102	.32699	94.82	5.18	....	90.53
J	6.5	.0294	.32927	96.26	3.74	....	72.69
K	7.0	.0547	.33174	100.	0.	....	49.19
L	8.0	.1019	.33231	100.	0.	....	5.35

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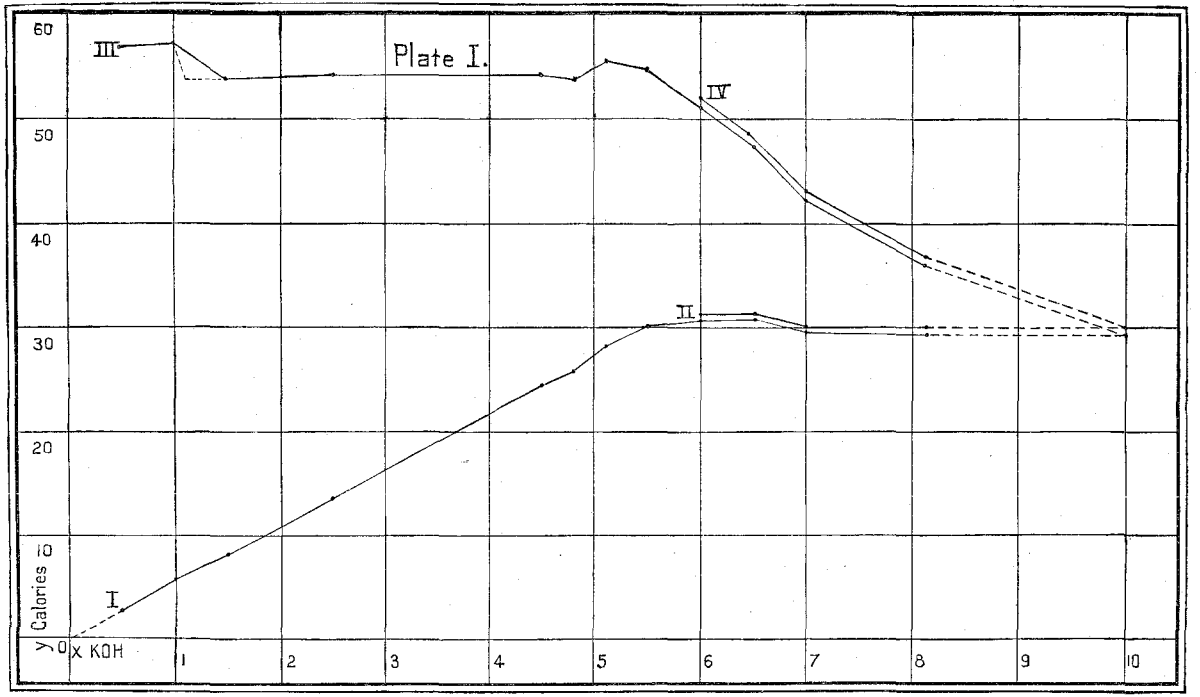

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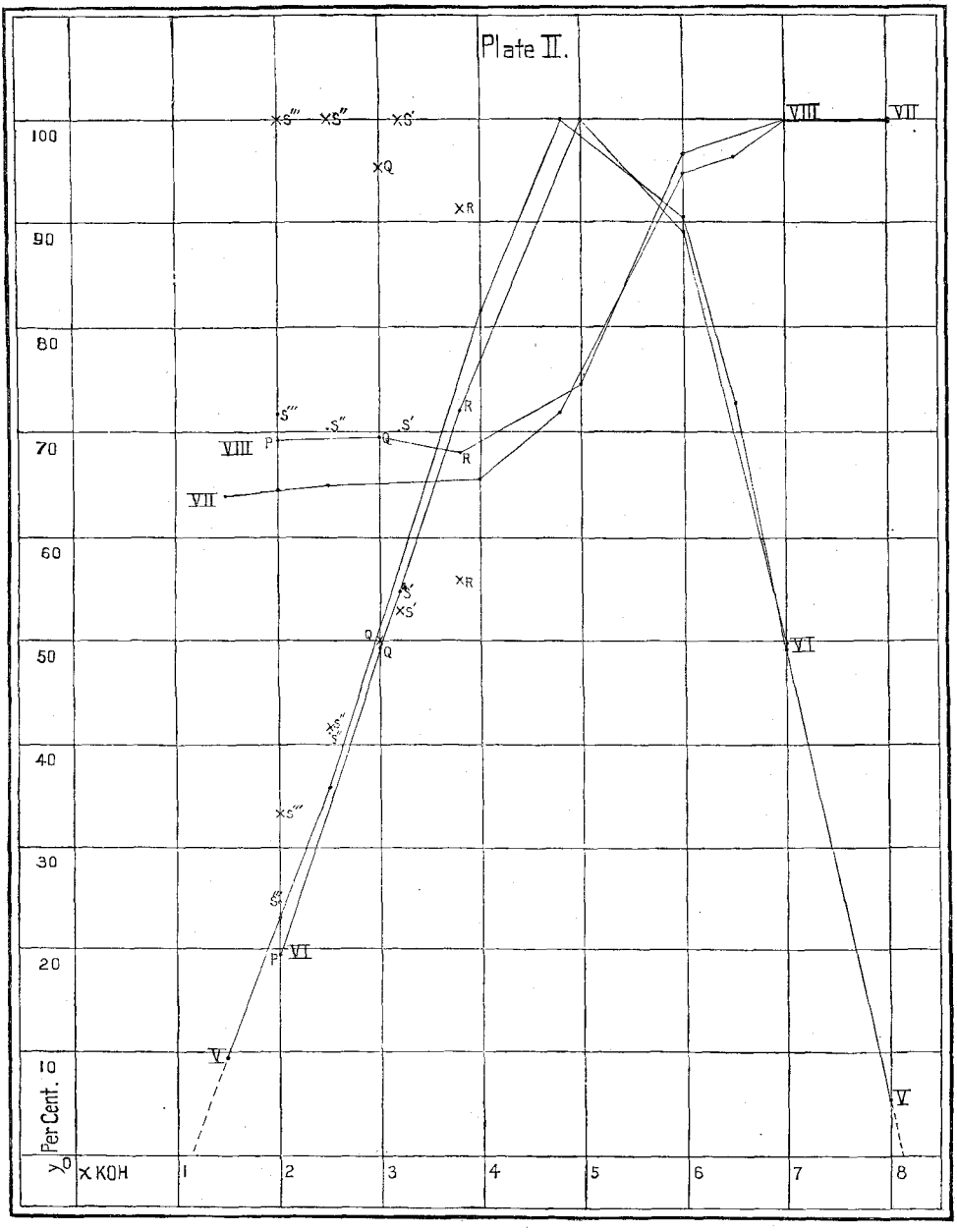

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TABLE VII. — ANALYSES.

(1 Alum + 10 KOH) + x H_2SO_4.

Exp.	x.	Grm. Al_2O_3 found in 50c.c. of Filtrate.	Grm. SO_3 found in 50c.c. of Filtrate.	Al_2O_3 in 100 pts. of Prec.	SO_3 in 100 pts. of Prec.	K_2O in 100 pts. of Prec.	Per cent of total Al_2O_3 in Prec.
N	1.5	.0540	.45788 cal. .45679 found.	100.	0.	....	49.84
O	2.0	.0119	.50011 cal. .49673 found.	96.59	3.41	....	88.95
T	2.5	.0	.33231 cal. .29512 found.	74.33	25.67	0.	100.
P	4.0	.0867	.66969 cal. .66036 found.	69.20	30.80	....	19.47

TABLE VIII. — ANALYSES.

1 Alum + x KOH.

Exp.	x.	Grm. Al_2O_3 found in 50c.c. of Filtrate.	Grm. SO_3 found in 50c.c. of Filtrate.	Al_2O_3 in 100 pts. of Prec.	SO_3 in 100 pts. of Prec.	K_2O in 100 pts. of Prec.	Per cent of total Al_2O_3 in Prec.
Q	3.0	.0547	.30898	69.42	30.58	....	49.19
R	3.8	.0300	.29598	68.13	31.87	....	72.13
S'	3.2	.0516	.13951	70.11	29.89	....	54.78
S''	2.5	.0543	.15017	70.33	29.67	....	41.11
S'''	2.0	.0608	.15835	71.74	28.26	0.	24.57

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IX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

CRYSTALLOGRAPHIC NOTES.

By Oliver W. Huntington.

Communicated by the Corresponding Secretary, June 10, 1885.

Crystals of Azurite from Arizona.

The mineral cabinet of Harvard College has recently received, through the kindness of Mr. Godfrey Hyams, some very interesting groups of azurite crystals. The specimens came from the mines of the Detroit Copper Company, situated near Clifton in the extreme eastern portion of Arizona, and I am indebted to Mr. Hyams for the following description of their occurrence.

"The formation in which the deposits are situated is peculiar to these mines, so far as I know. The zones or belts of copper occur in a sort of felsite on a contact between lime and iron, the lime being calcite and the iron an oxidized compound of varying composition. Specimens analyzed have given results which show that hematite, limonite, turgite, and clay iron-stone all occur.

"The ore appears in different forms: —

"1. Malachite, as fibrous, botryoidal, stalactitic, encrusting, and massive.

"2. Azurite, fibrous, botryoidal, encrusting, massive, and lastly crystallized.

"The crystals occur in various ways; singly on or in different manganiferous clays, in clusters like stilbite, in plates like nail-head spar, and in columns around a central axis like rock-candy.

"The two carbonates are in every phase of transition. We have malachite changing into azurite, that is, the malachite outside and azurite inside, then the reverse, malachite pseudomorph after azurite, and *vice versa*. Then again specimens of native copper occur in parts covered with crystals of cuprite, and these crystals in turn incrusted with malachite. With these are also large masses of cuprite,

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chrysocolla, and some native copper, but as yet, even at a depth of over two hundred feet, no sulphides have been discovered, — a condition which is very unusual.

"There is another form in which the azurite is found, which resembles the Chessy deposits, that is, in a quartzose rock scattered in nuggets varying from the size of a pea to that of a walnut. All the ores carry, besides iron and silica, a small percentage of manganese and alumina, together with an amount of zinc varying from two to eight per cent."

The specimens received at the cabinet of Harvard College consisted of large masses of transparent crystals closely packed together, accompanied by beautiful stalactites consisting mainly of azurite, but coated over with malachite, the malachite usually covering the azurite.

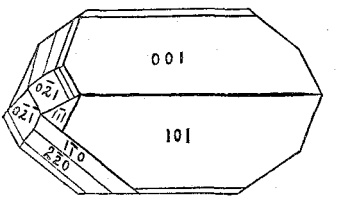

Fig. 1.

Many of the crystals resemble closely those from Chessy, being grouped together so as to give a general rhombohedral aspect, having rounded faces and looking not unlike saddle-back crystals. These saddle-back crystals were all more or less rough, dull, and opaque; but with them were associated numerous brilliant transparent glassy crystals elongated on the ortho-diagonal, having the general aspect shown in the accompanying sketch (Fig. 1).

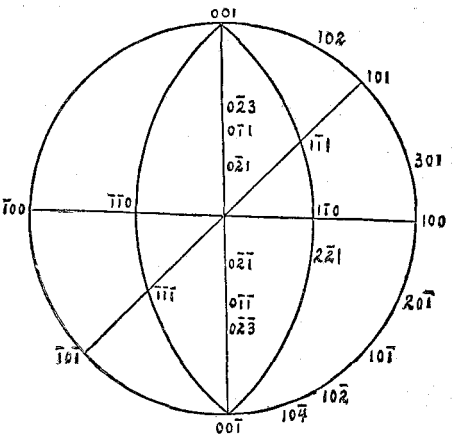

Fig. 2.

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These crystals presented no new planes, and corresponded in their crystallographic elements so closely with those given by Des Cloizeaux that it seemed best to refer the planes to the same axial dimensions. The measurements were made with a reflecting goniometer, having a micrometer screw graduated to ten seconds; but since the planes were usually rounded or badly striated, the reading could only be accurately made in comparatively few cases, and in the table below the best angles have been indicated by heavy-faced type.

$C = 87° 39'$. $c : b : \dot{a} = 1.0378 : 1.1807 : 1$.

ORTHO-DIAGONAL ZONE.

	DES CLOIZEAUX.	
$001 \wedge 102$	27° 55′	26° 35′
$001 \wedge 101$	47° 6′	**47° 3′**
$001 \wedge 301$	74° 20′	**74° 20′**
$001 \wedge 100$	92° 21′	92° 33′
$100 \wedge 20\bar{1}$	25° 16′	26° 8′
$100 \wedge 10\bar{1}$	42° 48′	43° 15′
$100 \wedge 10\bar{2}$	59° 44′	64° 28′
$100 \wedge 10\bar{4}$	73° 16′	70° 51′
$00\bar{1} \wedge 10\bar{4}$	14° 23′	17° 19′

CLINO-DIAGONAL ZONE.

	DES CLOIZEAUX.	
$001 \wedge 0\bar{2}3$	30° 21′	31° 31′
$001 \wedge 0\bar{1}1$	41° 17′	40° 22′
$001 \wedge 0\bar{2}1$	60° 21′	60° 37′
$0\bar{2}1 \wedge 02\bar{1}$	59° 18′	**59° 7′**

PYRAMIDAL ZONE.

	DES CLOIZEAUX.	
$001 \wedge 1\bar{1}1$	54° 40′	54° 44′
$001 \wedge 1\bar{1}0$	91° 48′	**91° 48′**
$1\bar{1}0 \wedge 2\bar{2}1$	19° 58′	19° 46′
$2\bar{2}1 \wedge 00\bar{1}$	68° 13′	68° 28′

VERTICAL ZONE.

	DES CLOIZEAUX.	
$100 \wedge 1\bar{1}0$	40° 14′	40° 16′
$1\bar{1}0 \wedge \bar{1}\bar{1}0$	99° 32′	**99° 30′**
$\bar{1}\bar{1}0 \wedge \bar{1}00$	40° 14′	**40° 15′**

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OBLIQUE ZONE.

DES CLOIZEAUX.

$101 \wedge 1\bar{1}1$	31° 53′ 30″	**31° 55′**
$1\bar{1}1 \wedge \bar{1}\bar{1}\bar{1}$	116° 13′	**116° 18′**
$\bar{1}\bar{1}\bar{1} \wedge \bar{1}0\bar{1}$	31° 53′ 30″	**31° 50′**

The planes of the main prism zone parallel to the ortho-diagonal, and those of the clino-diagonal zone, were very badly striated, and somewhat rounded, so that most of the measurements were made from mere flashes, only three of the angles being sharply defined. The remaining three zones were more sharply defined, and it will be noticed that in these zones the measurements more nearly coincide with those of Des Cloizeaux, and in every case they coincide within the probable limit of error due to the irregularity of the planes.

Quartz Twins.

In the September number of the American Journal of Science, Prof. W. G. Brown of the University of Virginia describes a group of twin crystals of amethystine quartz from Albemarle County, Virginia, which appear to resemble in structure twins originally described by G. Rose,* and which he interpreted as twinned parallel to the fundamental rhombohedron, although united by a plane perpendicular to the same rhombohedral face. It appears, however, as originally shown by Nauman,† that the structure of these groups might be interpreted as twins of the ordinary type, parallel to a rhombohedral face, $-\frac{5}{8}$ R, and the group examined by Professor Brown would seem to confirm this view, in so far as the corresponding rhombohedral faces of the twins are not absolutely in the same plane; although the irregularities he describes may obscure the small angular difference of twenty-six minutes, which could alone furnish decisive evidence as between the two theories under discussion.

Professor Brown also refers to the view of Ecle,‡ strengthened by the observations of Rath and Frenzel,§ and that of E. S. Dana,‖ that

* Poggendorf's Annalen, lxxxiii. 461, 1851.

† Elemente der Mineralogie, 6th ed., p. 190, 1864.

‡ Zeitschr. d. deutsch. geol. Gesellschaft, xviii. 428, 1866.

§ Poggendorf's Annalen, xvii. 155, 1875.

‖ American Jour. of Science, III., xii. 448, 1876, and Zeitschr. für Krystall., i. 39, 1877.

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similar twins might result from the growth of quartz crystals on a nucleus of calcite.

Through the kindness of Professor Brown the writer had an opportunity of measuring and studying the specimen from Albemarle County, Virginia, and he was thus led to measure with accuracy all the similar groups of quartz crystals in the mineral cabinet of Harvard College, and the following observations may be of value as additional evidence in regard to the phenomena in question. Out of a very large number of apparent twins, there were only three in which faces on any two individuals fell absolutely into the same zone, and in which an assumed plane of twinning could be referred, within the limits of error, to probable axial ratios.

The measurements on these crystals were as follows: —

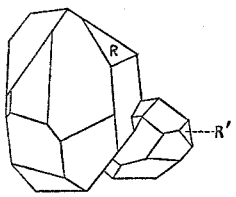

Fig 3.

In the accompanying sketch (Fig. 3), we have R and R' in the same zone, and $R \wedge R' = 21° 32'$. Axial divergence $= 125° 6'$.

We find from this, that the assumed twinning plane would be a rhombohedral face with the axial ratio 0.4488, and this compared with the known fundamental ratio 1.0999 corresponds almost absolutely to a negative rhombohedron, $-\frac{9}{2}\frac{9}{2}$.

With the group of crystals shown in Fig. 4 the same zone was measured, giving $R \wedge R' = 50° 26'$. Axial divergence $= 153° 59'$. Axial ratio for assumed plane of twinning $= 0.19994$. This compared with the fundamental ratio corresponds exactly to the negative rhombohedron $-\frac{2}{1}\frac{}{1}$.

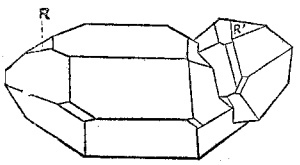

Fig. 4.

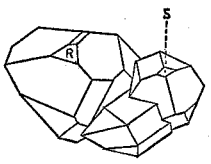

Fig. 5.

The group of crystals, Fig. 5, differed from the previous ones in having a plane of the direct hexagonal pyramid of one individual, and a plane of the indirect pyramid of the other, in a zone with the axes.

$R \wedge s = 14° 44'$. Axial divergence $= 117° 59'$. Axial ratio of assumed plane of twinning $= 0.3850$. And this corresponds absolutely to the negative rhombohedron $-\frac{7}{2}\frac{}{6}$.

The examples here given show a wonderfully close coincidence with possible though somewhat complex ratios, but it must be re-

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membered that these are only three out of a very large number of apparent twins, in which no such relation could be established. The following will serve as an illustration.

A group of crystals was found differing from the previous ones in no essential respects, in which R and R' were in a zone with the principal axes, making an angle with each other of 4° 8′. This would correspond to a twinning plane with an axial ratio of 0.63267, which bears no assignable relation to the fundamental rhombohedron. In other cases the approximation to possible ratios was much closer than this; but in most instances the planes on the two crystals were not even in the same zone, and every variation was noticed, from examples in which the reflected images would fall within the field of the telescope of the goniometer to those in which there was a much wider divergence, the crystals being displaced to a greater or less extent on the plane of twinning.

It will be seen by the above examples that in some cases the direct pyramid is in the same zone with the direct pyramid on the twin crystal, and in other cases it is in the same zone with the indirect; but intermediate positions were noticed, which would result from a greater or less rotation of one of the crystals on its own axis.

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X.

TELESCOPIC SEARCH FOR THE TRANS-NEPTUNIAN PLANET.

By David P. Todd, M. A.

Communicated June 10, 1885.

In the twentieth volume of the American Journal of Science, at page 225, I gave a preliminary account of my search, theoretic and practical, for the trans-Neptunian planet. I say *the* trans-Neptunian planet, because I regard the evidence of its existence as well founded, and further, because, since the time when I was engaged upon this search, nothing has in the least weakened my entire conviction as to its existence in about that part of the sky assigned; while, as is well known, the independent researches in cometary perturbations by Professor Forbes conducted him to a result identical with my own, — a coincidence not to be lightly set aside as pure accident.

That five years have elapsed since this coincidence was remarked, and the planet is still unfound, is not sufficient assurance to me that its existence is merely fanciful. In so far as I am informed, this spot of the sky has received very little scrutiny with telescopes competent to such a search; and most observers finding nothing would, I suspect, prefer not to announce their ineffective search.

The time has now come when this search can be profitably undertaken by any observer having the rare combination of time, enthusiasm, and the necessary appliances. Strongly marked developments in astronomical photography have been effected since this optical search was conducted; and the capacity of the modern dry-plate for the registry of the light of very faint stars makes the application of this method the shortest and surest way of detecting any such object. Nor is this purely an opinion of my own. But the required apparatus would be costly; and the instrument, together with the services of an astronomer and a photographer, would, for the time being, be necessarily devoted exclusively to the work. While, however, the photographic search might have to be ended with a negative result, in so far as the trans-Neptunian planet is concerned. there would still remain the series of

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photographic maps of the region explored, and these would be of incalculable service in the astronomy of the future.

In the latter part of the paper alluded to above, I state the speculative basis upon which I restricted the stellar region to be examined; also the fact that between November of 1877 and March of 1878 I was engaged in a telescopic scrutiny of this region, employing the twenty-six inch refractor of the Naval Observatory. For the purposes contemplated, I had no hesitation in adopting the method of search whereby I expected to detect the planet by the contrast of its disc and light with the appearance of an average star of about the thirteenth magnitude. A power of six hundred diameters was often employed, but the field of view of this eyepiece was so restricted that a power of four hundred diameters had to be used most of the time. I say, too, that, "after the first few nights, I was surprised at the readiness with which my eye detected any variation from the average appearance of a star of a given faint magnitude: as a consequence whereof my observing-book contains a large stock of memoranda of suspected objects. My general plan with these was to observe with a sufficient degree of accuracy the position of all suspected objects. On the succeeding night of observation they were re-observed; and, at an interval of several weeks thereafter, the observation was again verified." Subjoined to the original observations are printed these verifications in heavy-faced type.

In conducting the search, the plans were several times varied in slight detail, — generally because experience with the work enabled me to make improvements in method. Usually I prepared every few days a new zone-chart of the region over which I was about to search; and these charts, while containing memoranda of all the instrumental data which could be prepared beforehand, were likewise so adjusted with reference to the opposition-time of the planet as to avoid, if possible, its stationary point. The same thing, too, was kept in mind in selecting the times of subsequent observation. Notwithstanding this precaution, however, it would be well if some observer who has a large telescope should now re-examine the positions of these objects.

Researches in faint nebulæ and nebulous stars appearing likely to constitute a separate and interesting branch of the astronomy of the future, it has seemed to me that the astronomers engaged in this work may like to make a careful examination of some of the stars entered in my observing-book under the category of "suspected objects." The method I adopted of insuring re-observation of these objects was by the determination, not of their absolute, but only of their relative positions,

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through the agency of the larger "finder" of the great telescope. This has an aperture of five inches, a power of thirty diameters, and a field of view of seventy-eight minutes of arc. Two diagrams were usually drawn in the book for each of these objects, — the one showing the relation of adjacent objects in the great telescope, and the other the configuration of the more conspicuous objects in the field of view of the finder. Adjacent to these "finder" diagrams are the settings, — to the nearest minute of arc in declination, and of time in right ascension, — as read from the large finding-circles, divided in black and white. The field of view of the finder is crossed by two pairs of hair-lines, making a square of about twelve minutes on a side by their intersection at the centre. The diagrams in all cases represent the objects as seen with an inverting eyepiece. As the adjustment of the finder was occasionally verified, as well as the readings of the large circles, there should be no trouble in identifying any of these objects, notwithstanding the fact that no estimates of absolute magnitude were recorded. The relative magnitudes, while intended to be only approximate, are still shown with sufficient accuracy for the purpose of the research, and the diagrams are, in general, faithful tracings from the original memoranda.

I transcribe the observing-book entire.

Telescopic search for trans-Neptunian planet, with 26-inch equatorial.

1877, Nov. 3.7. — Clamping polar axis, swept in declination, intending to detect planet by its supposed disk. Using power of 600, swept along plane of orbit, from long. 155° to 166°.

An object with slightly planetary look seen in α $10^h\ 27^m$, $\delta + 10°\ 0'$.

An object (nebulous and about $5''$ in diameter) found in α $11^h\ 9^m.5$, $\delta + 5°\ 28'$:

[i]

It follows a star a $44^s.3$; and precedes b 69^s; c 70^s.

Nov. 4.7. — Searching by same method, v, 148° — 163°. Power 600. Soon clouded over.

Nov. 6.7. — Attempted method of survey by recording R. A.'s of stars in narrow zones, estimating δ and magnitude which were recorded by Townsend. Success not satisfactory — chronograph gave trouble. Then went on with sweep in declination, using power 400. $v = 163°$

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to 168°. Looked again for nebulous object seen Nov. 3.7. It has not moved. It is likely a nebulous star — a glistening point of light is seen from time to time in its centre.

Nov. 7.7. — Again tried method of search by recognition of disk. Improved by having dome all dark. I set with tangent screw in declination upon successive narrow zones, and sweep in R. A. Used power 600. Success good — shall try this method further. Clouded over between 16 and 17 hrs.

Nov. 11.7. — Swept carefully between 9° and 10° of my *plan* of to-day. Used power 600.

An object suspected, $+9°\ 45'$.

[ii]

Object is *c*. $ab = 24^s \pm$

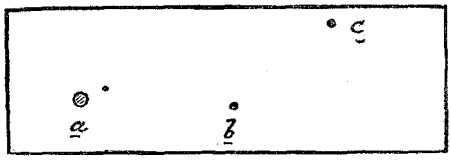
$ac = 74^s \pm$

R. A. $10^h\ 19^m \pm$

I do not much believe it to be anything but a star.

Examined again, Nov. 13.7. Object a star.

An object *a* about equally suspected, $+\ 9°\ 35'$, R. A. $= 11^h\ 1^m$. It has a faint companion, $p = 96°$, $s = 25''$.



[iii]

$ab = 12^s.5$. *c* is bright star and $2' \pm$ south of parallel of *b*.

Examined again, Nov. 13.7. Object a star. Twilight, however, prevented my seeing the comes.

Iris ⑦ Nov. 11. $\alpha = 3^h\ 43^m$, $\delta = +\ 24°\ 50'$.

After it began to be pretty light (about $17^h.5$), I tried search by clamping in R. A., and sweeping in declination, following my adopted plane of the planet's orbit.

Set on $\delta = +6°.5$.

$\alpha = 11^h\ 12^m$.

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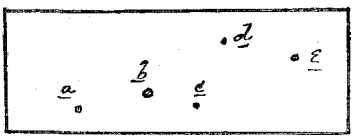
Suspected more fully an object which was too faint in the twilight to be compared with other stars near by. The instrumental position was, $\alpha = 11^h\ 20^m.5$, $\delta = +5°\ 8'$.

Tried power 890 on it, but did not get much of a disk. Look at this again.

Nov. 12.7. — Swept (not so satisfactorily as yesterday) between 9° and 8° 30′. Seeing not first rate. Used power 600. Faint nebula (probably) as follows, at *b*:



[iv]

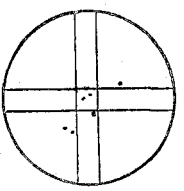
ab 9ˢ.7.
bc 5.3.
cd 2′±.
de 2′±.

Instrumental position, α $10^h\ 43^m.5$; δ +8° 58′.

$10^h\ 43^m$.

+8° 50′.

5-inch finder, thus:

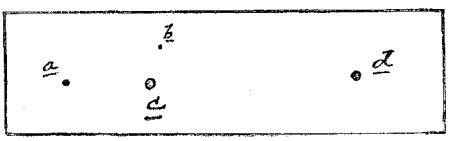


Examined again Nov. 13.7. Twilight prevented my seeing *b* and *d*. Look at this once more.

Examined again Dec. 2.7. *b* nebulous, but now plainly not round. Outline oblong, and jagged. It is a fixed object.

Nov. 13.7. — Good morning's work. Swept according to plan, from +8° 30′ to +7°, only shortening the zones a little. An object which may be only a faint nebulous star at *c*.

Instrument $\alpha = 10^h\ 48^m$; $\delta = +8°\ 30'$.



[v]

$ac = 21^s$.
$ad = 57^s$.

b is faint companion to *c*, about 2′ distant, and $p = 177°$. *d* is bright, and 1′ south of *c*.

Nov. 17.7. — Searched a short time for objects seen on the 12th and 13th. Was bothered variously, and search was ineffectual. Try again. Moonlight seems to interfere some. I think the object seen on the 13th is not now there.

Nov. 20.7. — Searched for object seen on the 12th. Either it is not now in the position then indicated, or (more likely) the full-moon

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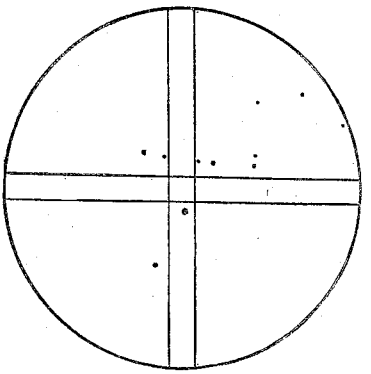
light prevents my seeing it. Try again, after the moon is out of the way — about Dec. 2.

Nov. 30.7. — Began search for object seen on 13th. Using power 600, swept carefully from $+8°\ 40'$ to $+8°\ 15'$ — zones about $3'$ wide and 20^m long. Could find nothing at all nebulous, like what I saw on the 13th. No moon present. I then tried power of 400, and at about $16^h.5$ hit on very faint object *a*. It is not at all like a faint star; but has a disk of nearly uniform illumination. So I compare it as follows, with one star preceding, and two following:

[vi] $ab = 34^s.$ $ac = 17^s.$ $cd = 14^s.$

Instrumental position $\left\{\begin{array}{l} a\ 10^h\ 45^m \\ \delta\ +8°\ 36' \end{array}\right\}$ painted circles.

The stars in the five-inch finder are these:

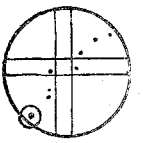


Some daylight at $17^h.7$, but could not then see *a*. Looked also for object seen on Nov. 12, but could not see it.

Dec. 2.7. — Settled all doubt about object seen on Nov. 12. Searched with power 400 for object seen on 13th, from $+8°\ 50'$ to $+8\ 15$. Zones $20^m\pm$ long. Could find nothing. Either the object is not now there, or it is much less easily recognizable than I supposed when I recorded so few stars near it. Shall now go on with the regular search.

Dec. 3.7. — Object *b* not like star, though I cannot see a disk well.

[vii]



$a = 11^h\ 0^m.$ $\delta = +7°\ 10'.$

$ab = 36^s.5$. *a* is north of *b* about $1'$. $bc = 4'$.

See Dec. 11.8. Also Dec. 12.7.

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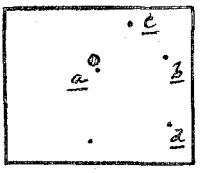
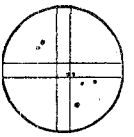
Object a suspected — it has a companion, $p = 25°$.



[viii] $ab = 6^s.7.$
$bd = 2'.5.$



$\alpha = 10^h\ 59^m.$
$\delta = +6°\ 42'.$

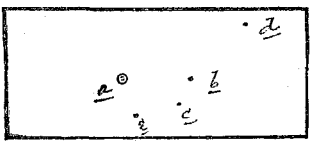
Swept with power 400, from 7° to 6° of plan of Nov. 11.

Dec. 11.8. — Objects a and companion are fixed. Same Dec. 12.7.

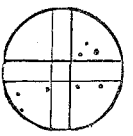
Dec. 7.7. — Came over to observatory, but found dome disabled so that I could not go on with my work.

Dec. 9.7. — Began search from +6°, south. Soon clouded up. Setting for next morning is +6°, exactly. Began to look for objects seen Dec. 3.7; but clouds too dense to permit their being seen. Power 400.

Dec. 11.7. — Searched with power 400, from 6° to +4° 10′. An object a suspected.



[ix]



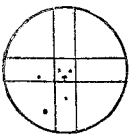
$ab = 8^s$ (10^h, s. t.).
$bc = 1'.5.$
$ce = 3'.$
$bd = 5'.$
$ab = 8^s.4$ (11^h, s. t.)

$\alpha = 11^h\ 20^m.$
$\delta = +4°\ 48'.$

Dec. 14.7. — a is a very faint and small nebula. 1878, Feb. 11.7. — Did not succeed in seeing a.

Termination of search — a star in setting $\alpha = 11^h\ 30^m$, $\delta = +4°\ 10'$.

Finder.



Equatorial, Power 400.

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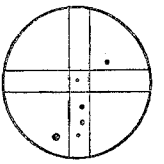
Hunted up objects seen on Dec. 3.7. The first one has moved; or, at least, pointing as then indicated with the finder, I found objects in about the position of *a* and *b*, which I suppose to be the same — though daylight prevents saying certainly. These second objects are on the same parallel, and distant $32^s \pm$. *c* was also seen.

Dec. 12.7. — Examined objects seen on Dec. 3.7. The second one, fixed. The first one — I cannot decide whether it has moved since yesterday or not, as I had no opportunity then of observing it accurately. The setting for it is, better, this: —

$a = 11^h\ 0^m.$
$\delta = +7°\ 17'.$



5-in. finder.

I now proceed to observe it accurately in R. A., and find by 14 chronographic transits that *b* follows *a* by $31^s.92$, at $10^h.3$, s. t.

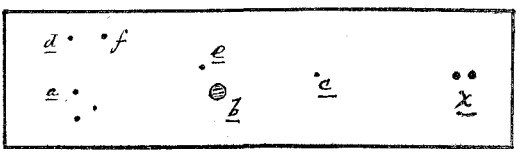
b is south of *a*

64.24
67.0
$2^r.76 =$ $''$

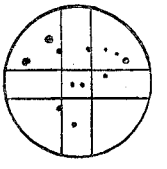
The object-glass is somewhat dewed; but I can see a companion to *b*, faintly — can only estimate: — $s = 20'' \pm$.
$p = 43° \pm$.

Dec. 14.7. — Mean of 3 chronograph transits, *a* precedes *b* $31^s.88$. The companion to *b* is visible. I conclude that *b* is a fixed star: I have not at any time seen the trace of a disk on it. Curiously enough, there is a group of stars nearly south of this, about 10′, which have nearly the same relative positions and magnitudes (except that *a* is much smaller). I think I must have observed this on Dec. 3.7 though I shall not now spend time to see. I believe also that *ab* is more than $36^s.5$, somewhat.

Go on with regular search — from $+4°\ 10'$ to $+3°\ 50'$. (Object *b* large and nebulous.)



[x]



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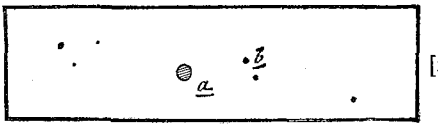
$ab = 21^s.7.$ $\quad a = 11^h\ 38^m.$
$bc = 5'.$ $\quad \delta = +3°\ 50'.$
$ad = 3'.$ $\quad x =$ object in centre of field of finder.
$be = 2'$ $(p = 210° \pm).$ (Power 400.)

Search of this morning ends with this parallel.

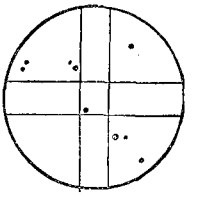
1878, Feb. 11.7. — Object *b* fixed. Instead of "large and nebulous," I should now record small, quite condensed, somewhat nebulous, and faint.

Dec. 19.8. — Bright light of moon, nearly full. Also some clouds passing. Attempted verification of object seen on 14.7. Saw the two stars *x*; also *d*, *f*, and *c* without difficulty. *a*, and the two stars below it; also *e* and *b* were not visible.

Dec. 27.8. — Object *b*, seen on the 14th is fixed — probably a faint nebula. Going on with regular search, I suspect an object *a:* it has a small, but poorly defined disk.



[xi]



Power 400.
$ab = 7^s.0$ (from a few eye-and-ear transits).

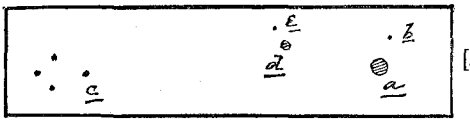
$a = 11^h\ 56^m.$
$\delta = +2°\ 37'.$
Finder.

1878, Feb. 6.6. — Object fixed.

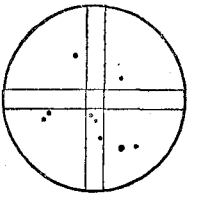
Search of this morning ends with this parallel. Search not wholly satisfactory, as light of moon, one day past last quarter, interfered some. Still, think I missed nothing.

1878, Jan. 2.7. — Object *a* seen Dec. 27.8 is fixed. Farther south I find an object which is large and nebulous. Marked *a*. *d*, small, faint, and nebulous.

Finder.



[xii]



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$\triangle a$.

$ab = 2^s.1$ $(15^h\ 55^m)$.

$cb = 63^s$.

$ad = 23^s.1$.

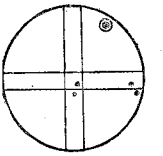
b and c should be nearly on the same parallel.

$\triangle \delta\,(ab) = 2'.5$. $s\,(ed) = 1'.5$.

1878, Feb. 6.6. — d and a fixed.

Another pair of objects:

[xiii]



b large and nebulous. e suspected somewhat.

a precedes b $0^s.2$.

b precedes c 5.7.

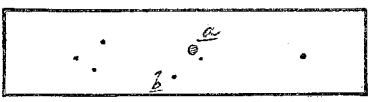
d precedes e 1.4.

All these objects are far from my adopted plane of orbit of trans-Neptunian planet.

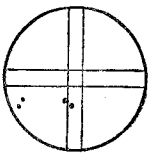
1878, Feb. 6.6. — b and e fixed.

Jan. 5.7. — All four of the objects seen Jan. 2.7 are fixed. They are worth looking at again after two or three weeks, as they are near the present stationary point.

Another object, a, slightly suspected.

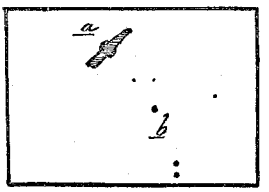


[xiv]



Definition so poor that it may be only a star blurred.

Finder.



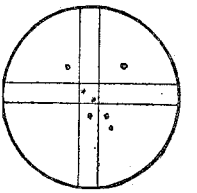
[xv]

$a = 12^h\ 5^m$.

$\delta = +2^\circ\ 0'$.

a precedes b $5^s.5 \pm$

(at $5^d\ 17^h\ 40^m$).



1878, Feb. 5.6. — Object fixed.

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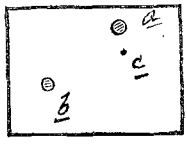
Object *a* has appearance of an elongated nebula. Beside the central condensation there is a minor and less marked one in the northern extremity (preceding).

Went on with regular search — that for this morning terminating with the above parallel, $+2^\circ\ 0'$.

Jan. 6.7. — At 16^h, elongated object above precedes about $5^s.1$, by eye-and-ear transits, roughly taken. Must observe it accurately on chronograph. The central condensation is not very sharp.

Object at bottom of preceding page [xiv] does not seem to be anything but a star with faint nebulous border. In fact, the one below it (and preceding), *b*, looks exactly like it.



[xvi]

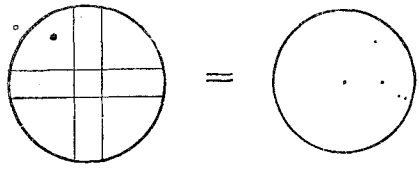
$ac = 45''$ (est.).
$ab = 1'.7$.
$\angle acb = 96^\circ$.
p (c to b) $= 125^\circ$.

Look at this again, after a week or so.

1878, Feb. 6.6. — Objects fixed.

Went on with regular search. Nothing suspected. Employed power 400. Search terminates with 4 mag. star in finder, thus : —

$\alpha = 12^h\ 14^m$.
$\delta = +0^\circ\ 15'$.



For parallel of end of this morning's search.

Battery out of order — cannot use chronograph. So observed object at top of preceding page [xv] by eye and ear. Mean of several transits,

a precedes b $5^s.04$. $13^h\ 30^m$, s. t.

Measured $\triangle\ \delta$ with micrometer.
Fixed wire on *a*.

Movable wire on *b*, reads	55.62
	'49
Coincidence 64.14.	55.56
	64.14
a south of *b*	$8^r.58$
	$= 85''.35$.

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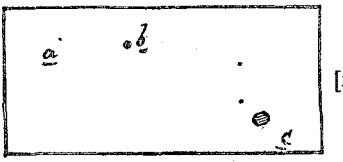
Jan. 11.7. — Object (elongated and nebulous) observed Jan. 5 and 6 is still at same distance as on the 6th, so far as a few eye-and-ear transits would decide. The preceding and northern "condensation," observed on the 5th, now appears as a faint star, apparently shining through that wing of the slender, elongated "nebula."

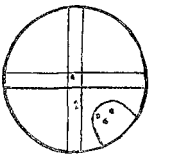
Went on with regular search, power 400. Found curious configuration of stars — 12 and 13 mag. They form a nearly perfect square (about 35″ on a side). On same parallel as η Virginis, and following it about 10^m.

c suspected object — faint and nebulous — outline quite regular.



[xvii]

$a = 12^h\ 18^m$.
$\delta = -0°\ 20'$.



Set rough circle at 0° so as to bring small triangle in centre of field of finder.

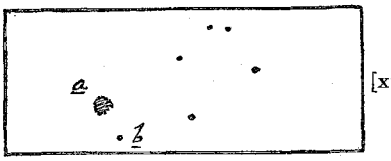
a precedes *b* $8^s.2 \pm$.
b precedes *c* $13^s.6 \pm 0^s.07$ at $17^h.5$.

1878, Feb. 5.6. — Object fixed.

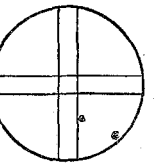
This morning's search terminates with this parallel.

Jan. 14.7. — Suspected object *c* (Jan. 11.7) fixed.

A nebulous cometary mass *a* (faint and irregular).



[xviii] $a = 12^h\ 9^m$.
$\delta = -0°30'$.

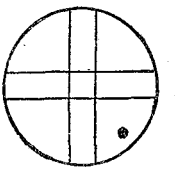


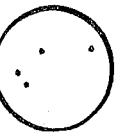
a precedes *b* $4^s.1 \pm$. Power 400.

1878, Feb. 6.6. — Object fixed.

Search ends (γ Virginis).

$a = 12^h\ 35^m$.
$\delta = -1°\ 10'$.





Elongated object first seen Jan. 5.7 is a nebula. I think it is Herschel (G. C. 2776).

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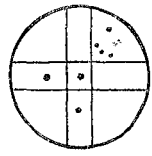
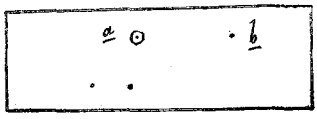
Feb. 5.5. — Began search — finder thus: —

$a = 10^h\ 9^m.$
$\delta = +13°\ 30'.$

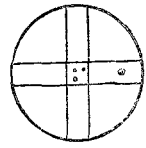


Power 400.
Object a suspected.

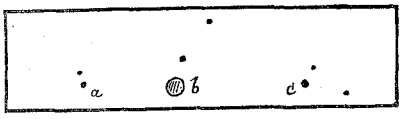


[xix]

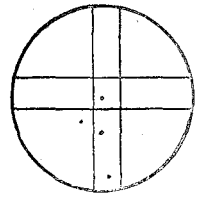
$a = 9^h\ 56^m.$
$\delta = +13°\ 25'.$



$ab = 25^s.3 \pm 0^s.1.$



[xx]

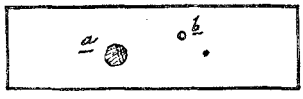


b very faint and diffused.
$ab = 32^s \pm.$
$bc = 43^s \pm.$

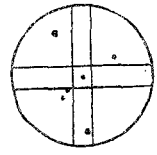
$a = 10^h\ 5^m.$
$\delta = +13°\ 18'.$

Came upon an object — finder: —

$a = 10^h\ 3^m.$
$\delta = +12°\ 55'.$



[xxi]



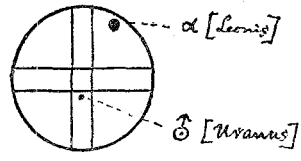
b pretty bright.
a quite faint, and seems to have a disk.
a precedes b (mean of 6 chronograph transits) $28^s.17$ at s. t. $11^h\ 12^m$.
a precedes b (mean of 9 chronograph transits) $28^s.35$ at s. t. $14^h\ 6^m$.

Feb. 6.5. — Object a (bottom of preceding page) [xxi] precedes b $28^s.39$ (mean of 10 chronograph transits, at m. t. $12^h\ 50^m \pm 10^m$.

Went on with regular search. Power 400.

Suspected object faint and diffused.

[xxii]



$ba = 86^s.$

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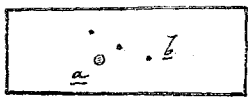
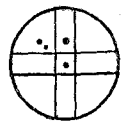
Object *a* small and quite faint.



$ab = 6^s.$ [xxiii]

$a = 10^h\ 6^m.$
$\delta = +12°\ 20'.$



1878, Mar. 5.6. — Object fixed.

Continue search from this setting of finder — beginning with parallel of the wide pair. $\delta = +12°\ 8'.$

Spent an hour or two in re-examining objects previously suspected. Notes accompany each object examined. Found all fixed — many small and faint nebulæ.

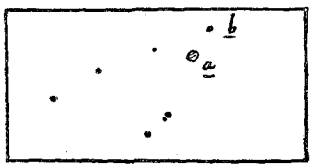
Feb. 11.6. — Object 10 lines above [xxiii], fixed — distance roughly 6^s, by disappearance-transits.

Object *a* (bottom preceding page [xxi]) precedes *b* $28^s.3$; (mean of two eye-and-ear transits). It still has the same appearance — very like that of a faint planet, with a small, ill-defined disk.

An hour or so in examining other objects previously suspected. Notes *loco*. Moon is beginning to interfere seriously.

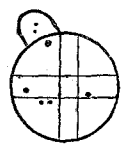
Feb. 26.5. — Began search with power 400, at parallel $+9°\ 30'$, going north.

Object *a* suspected — not a good disk — only regular and nebulous.

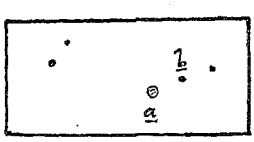


$\Delta\ a.$
$ab = 3^s.25.$ [xxiv]

$a = 10^h\ 31^m.$
$\delta = +9°\ 35'.$

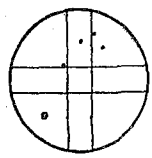


1878, Feb. 28.5. — Object fixed.



$ab = 1'.5.$ [xxv]

$a = 10^h\ 37^m.5.$
$\delta = +10°\ 45'+.$



a very faint, and but faintly suspected.

1878, Feb. 28.5. — Object fixed.

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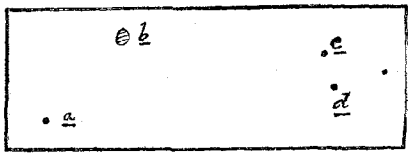
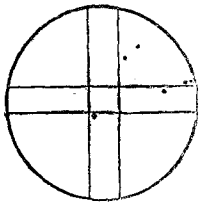


[xxvi]

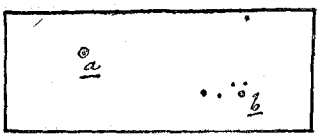


$ab = 7^s.9 \pm 0^s.1.$
$cd = 2^s.0.$

$\alpha = 10^h\ 30^m.$
$\delta = +10°\ 55'.$

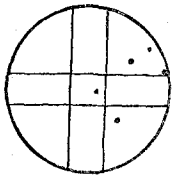
Morning's search terminates with this parallel.

Feb. 28.5. — Going on with search. Power 400. Verified places of objects seen Feb. 26.5.



[xxvii]

$\alpha = 10^h\ 15^m.$
$\delta = +11°\ 0'.$



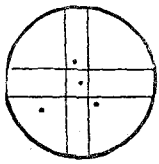
$\Delta\alpha\ (ab) = 27^s.15.$

a bright and very star-like — disk slightly suspected.

1878, Mar. 4.5. — Object fixed.

[xxviii]

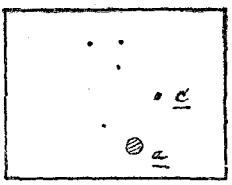
$\alpha = 10^h\ 30^m.$
$\delta = +11°\ 10'.$



a very faint — could not observe transits.

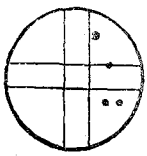
ac a little less than $\frac{1}{2}\ ad$ or $\frac{1}{2}\ cd$.

1878, Mar. 4.5. — Object fixed.



[xxix]

$\alpha = 10^h\ 15^m.$
$\delta = +11°\ 30'.$



a quite faint; and nebulous (regularly).

$\Delta\alpha\ (ac) = (7^s.0)\ ??$

1878, Mar. 4.5. — Object (probably) fixed.

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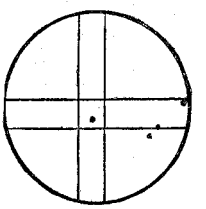
Morning's search terminates with this parallel.

1878, Mar. 4.6, $\Delta a\,(ac) = 5^s.2 \pm 0^s.1$. I feel quite sure that a has not moved: the Δa ($7^s.0$) was put down from memory on March 2, without much hope of its being right. But, judging from the configuration, I say that a has not moved appreciably.

March 4.5. — Proceeded with regular search (power 400) after verifying objects seen Feb. 28.5+.

[xxx]

$a = 10^h\ 26^m.5.$
$\delta = +11°50'.$



a like elongated nebula — rather faint. Centre of it about same R. A. as star b. I have represented it somewhat too far south — its centre should be nearer parallel of star c.

1878, Mar. 5.5. — Object fixed.

Morning's search terminates with this parallel.

Put up instrument all in order at 1.45 A. M. Cahill, watchman — told him to wake me at 6 A.M.

March 5.5. — Proceeded with regular search (power 400), after verifying object seen yesterday.

Happened upon a nebulous mass — central condensation quite sharp — in $a = 10^h\ 39^m$, $\delta = +12°\ 20'$. I take it to be G. C. 2194, and so do not observe its position accurately: it is very bright.

Completed this morning the zone which fills up the gap to $\delta = +12°\ 20'$ (see Feb. 6.5); and went still farther north — to $\delta = +12°40'$.

So that the adopted plane of orbit of trans-Neptunian planet is now searched (without break) from

$$v = 146°.8$$

to

$$v = 186.1.$$

Put up instrument all in order at 3 A. M., March 6, and went home at 3.45. Hayes, watchman in charge.

LAWRENCE OBSERVATORY, AMHERST, MASS.,
7 October, 1885.

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INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATION FROM THE RUMFORD FUND.

XI.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXII. — COLORED MEDIA FOR THE PHOTOGRAPHIC DARK ROOM.

By WILLIAM H. PICKERING.

Communicated May 13, 1885.

SINCE the advent of the gelatine dry plate, many photographers have complained that their eyes are injured by the dark red light generally used in development. Considerable discussion of this subject has been aroused of late, but the only experiments made, as far as can be learned, have been to determine how much plates fog when exposed at the *same distance* to the various media tried. The experimenter then examines some object at that distance, and if he thinks he can see it about as well, and the plate is less fogged, the medium is pronounced an improvement.

In order to obtain more satisfactory results the following problem was proposed: — For a given distinctness of vision, what medium, or combination of media, will give the least fog on a gelatine plate? In order to determine at what distance from the lights equal distinctness of vision was obtained, a negative having some fine markings upon it was held at such a distance from the various sources that the details were just distinguishable from one another. Different portions of a sensitive plate were then exposed at these distances, one after another, to light coming through the different media, and the plate was then developed. Exposures with both daylight and gas-light as sources were made on the same plate, and, as was to be expected, those made by daylight were much the most fogged. If more colored glass was used, the daylight was too faint. So, for this reason alone, gas-light would be preferred. Add to this, that, if the gas-flame be placed at the bottom of a properly constructed flue, it will serve to ventilate as

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well as light the dark room; and also that it can be used in the evening and on dark winter afternoons when daylight is out of the question. Moreover, since the gas-flame is much more uniform in brilliancy, it is correspondingly easier to determine when a plate is properly developed, and fewer plates are lost in this way.

Experiments with the following media have been made, and are numbered in the second and third columns in the order of their desirability. It will be noticed that there are five media which with gas-light give better results, i. e. less fog, than the best medium with daylight. In the second series the third column gives the distance in inches in each case at which the fine details were visible from the gas-flame. No medium is wholly satisfactory with daylight unless it contains red glass or paper. The window used with the gas-light measured six by seven inches, and was situated fourteen inches from the gas-flame. The window used with daylight measured five by five inches. Direct light from the clouds was used. The plate was developed in the first series with oxalate, and in the second with pyro and soda developer.

FIRST SERIES.

Colored Media.	Gas.	Sky.
Red and yellow glass	1	12
Red and ground glass	2	6
Post-office paper	3	14
Red glass	4	8
Yellow glass double	5	16
Yellow and violet glass	7	18
Carbutt's red paper	9	10
Red glass double	11	13
Yellow and green glass	15	17

SECOND SERIES.

Colored Media.	Gas.	Inches.
Canary paper double	1	8
Golden fabric double	2	29
Red glass	3	38
Golden fabric single	4	58
Red, yellow, and ground glass	5	11
Red and yellow glass	6	22
Canary paper single	7	19
Post-office paper	8	15
Yellow and green glass	9	41

It was found that ground glass transmitted fifty-five per cent of the light from a gas-flame coming through red glass, while it transmitted

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only about nine per cent of daylight under similar circumstances. Its effect is therefore similar to yellow glass. The fact that the yellow-violet combination was so satisfactory with the gas-flame was probably due to the capacity of the yellow to cut off the small amount of violet emitted by this source, while it was quite inadequate to destroy it in the case of daylight, as is indicated by the figures. The precise order here given is not insisted on, but only the general sequence, as in the case of most of the media there was very little difference in their desirability, and sometimes the position of two media on the list would be reversed by a negative. One fact was brought out, however, with great distinctness in all the series, and that was the great inferiority of the yellow-green combination. This was of course to be expected, but, as many photographers still use this medium in their dark rooms, it was considered desirable to include it in the list, merely to show its inferiority. Although in the second series Canary paper double seemed to give the least fog of any of the media, the light transmitted by it proved to be so faint that it was quite inadequate for satisfactory illumination of the dark room; and, owing to its opacity, some doubt was cast on the accuracy of the observation. The second medium on the list has therefore been selected as the best practical one to employ with gas-light illumination. Its color is very pleasant to the eyes, and being translucent, instead of transparent, it lights the whole room in a very satisfactory manner. It is advisable to place it behind a sheet of glass, in order to protect it from being soiled by the chemicals employed. If one is obliged to use daylight as a source of light, it is probable that a sheet of red glass in connection with one or two thicknesses of Golden fabric would form as satisfactory a combination as any.

Experiments were next made to determine how bright a light is permissible with the medium adopted. The fish-tail burner which was used on the gas-lamp was placed fourteen inches behind a double sheet of Golden fabric, measuring twenty-four by sixteen inches. An extremely sensitive gelatine plate was placed at a distance of twelve inches in front of the medium, and a portion of it exposed for one minute. It was found, that if the gas-flame measured only one inch in height, not the least trace of fog was produced by the exposure. This is too faint a light for satisfactory use, however, and as a very minute amount of fog does not injure a negative perceptibly, and the direct exposure to the light in actual practice is much less than a minute, the flame is turned up to a height of an inch and a half or two inches for ordinary development. By this light one can readily see to

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read the finest type, and the light pervading the whole room is very satisfactory. After a short exposure to it, in fact, it seems almost like white light.

In this connection may be mentioned a device which has proved very useful as an auxiliary in enabling one to judge of the proper development of a negative. A square hole measuring an inch and a half on a side is cut in the upper portion of the Golden fabric, and a piece of red glass inserted between the two thicknesses. If a negative be now held near this hole, a red square of light will be cast upon it. This square can be seen even when the lights of the negative are quite intense, and by noting its distinctness, one can judge of the opacity of the high lights as accurately as he can of the details of the shadows of the picture. If the high lights reach their proper intensity first, he develops for the shadows, and *vice versa.*

As the whole question of the proper medium to use resolves itself merely into what part of the spectrum to employ, red, orange, or orange-yellow, and all three of these yield nearly equally good results, it is evident that no important improvement can be made in the future. But as the orange-yellow is much the pleasantest light of the three, and seems to give rather less fog than either of the others, it is the color to be recommended. Any medium which will transmit this color will be found satisfactory, but Golden fabric is perhaps as convenient as any.

A very portable form of lantern to be used when travelling consists of a strip of Golden fabric a foot wide by two and a half in length. When one wishes to use it, it is rolled into a cylinder a foot long, and five inches in diameter, and pinned. A kerosene lamp with the wick turned down low, or a candle, is then placed inside, and the lantern is complete. The circle of white light formed on the ceiling is not bright enough to do any harm. The lantern is set several feet away from the exposed plates, and they should in general be protected as much as possible from direct illumination. There is then plenty of light, and yet not the slightest danger of fog.

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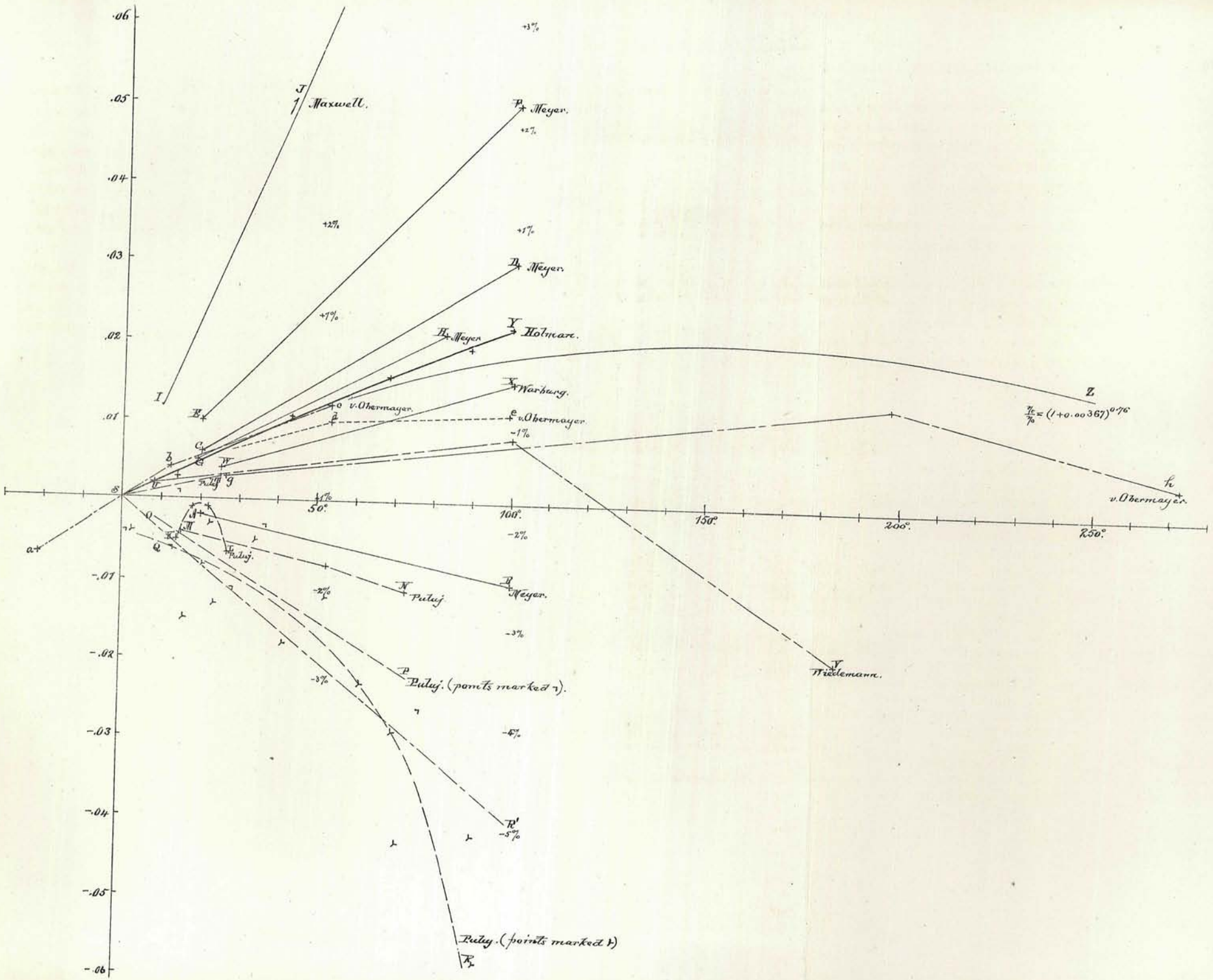

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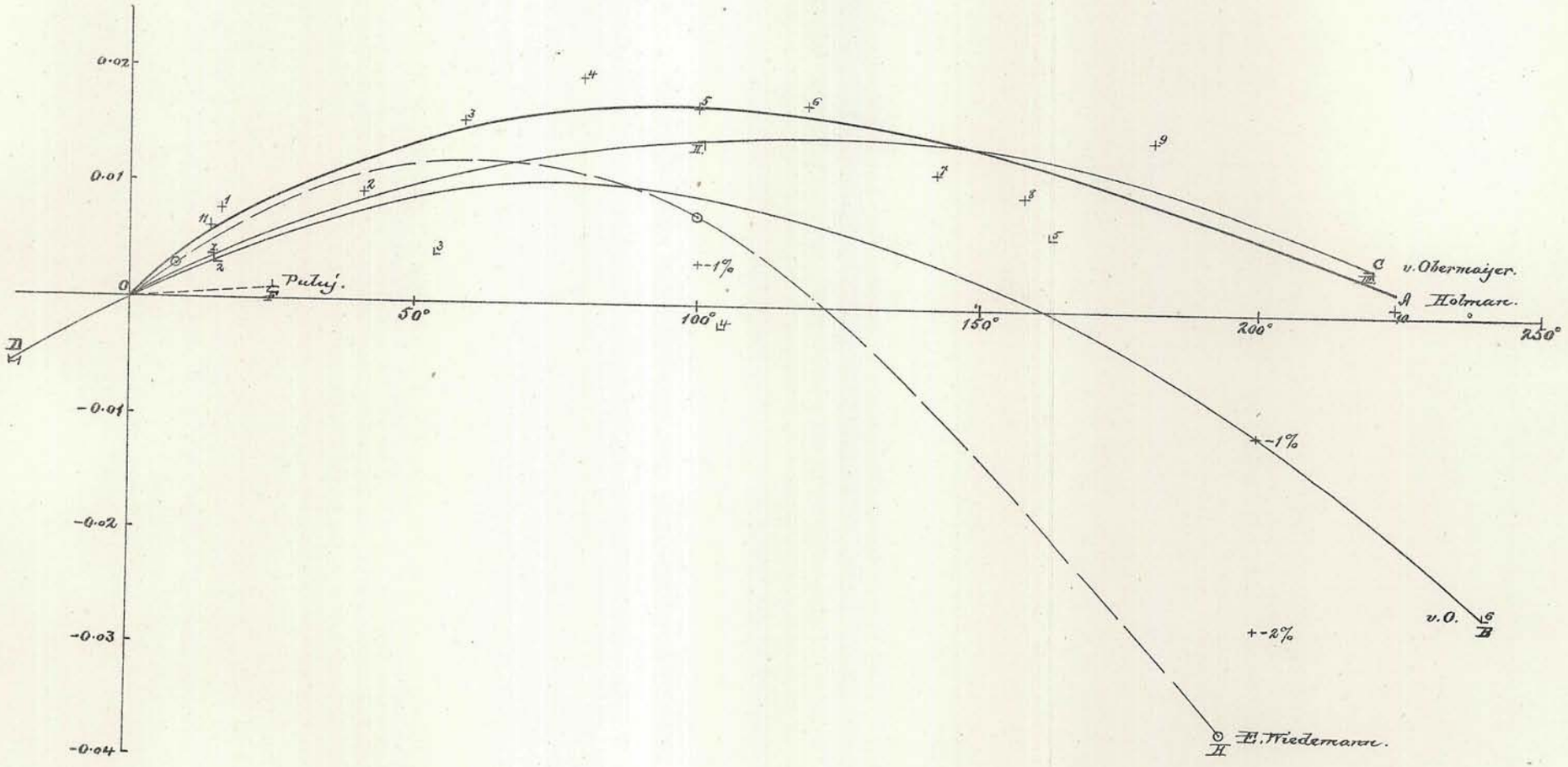

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